

UNITED STATES DISTRICT COURT
WESTERN DISTRICT OF WASHINGTON
AT SEATTLE

ACUSHNET COMPANY, a Delaware
corporation,

Plaintiff,

v.

COSTCO WHOLESALE CORPORATION,
a Washington corporation,

Defendant.

Case No. 2:17-cv-1214

**COMPLAINT FOR PATENT
INFRINGEMENT AND FALSE
ADVERTISING**

JURY TRIAL DEMANDED

Plaintiff Acushnet Company (“Acushnet Company”), by and through undersigned counsel, hereby submits this Complaint in this action for patent infringement and false advertising against Costco Wholesale Corporation (“Costco”), and states and alleges the following:

THE PARTIES

1. Acushnet Company is a Delaware corporation with its headquarters located at 333 Bridge Street, Fairhaven, Massachusetts 02719.

2. Upon information and belief, Costco is a Washington corporation with its principal place of business at 999 Lake Drive, Issaquah, Washington 98027.

COMPLAINT FOR PATENT INFRINGEMENT AND
FALSE ADVERTISING - 1
Case No. 2:17-cv-1214

130947.0001/7038566.1

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JURISDICTION AND VENUE

3. This case arises under the patent laws of the United States, 35 U.S.C. § 101 *et seq.* and the Lanham Act, 15 U.S.C. §§ 1051 *et seq.* Supplemental jurisdiction exists over Acushnet Company's state law claims pursuant to 28 U.S.C. § 1367(a).

4. This Court has subject matter jurisdiction over this case pursuant to 28 U.S.C. §§ 1331, 1332, 1338, and 1367(a).

5. Upon information and belief, Costco purposefully directs its activities toward this forum. Costco markets, advertises, offers to sell, sells and distributes infringing products, as described below, throughout the United States, including the Western District of Washington. Thus, Costco is subject to personal jurisdiction in this district.

6. Venue is proper in this district pursuant to 28 U.S.C. §§ 1391 and 1400(b). On information and belief, Costco has a regular and established place of business in this district, including its principal place of business at 999 Lake Drive, Issaquah, Washington 98027.

BACKGROUND

I. ACUSHNET COMPANY'S INDUSTRY-LEADING TITLEIST® GOLF BALLS

7. Acushnet Company is the global leader in the design, development, manufacture and distribution of performance-driven golf products, which are widely recognized for their quality and excellence. Acushnet Company is driven by its focus on dedicated and discerning golfers and the golf shops that serve them. Acushnet Company's mission—to be the performance and quality leader in every golf product category in which it competes—has remained consistent since Acushnet Company entered the golf ball business in 1932. Among Acushnet Company's many industry-leading products are golf balls sold under the Titleist® brand name, including its Titleist® Pro V1® and Pro V1x® golf balls.

1 8. Acushnet Company has three company-owned golf ball manufacturing facilities
2 encompassing over 600,000 total square feet. Acushnet Company works hard to ensure that its
3 golf ball products are manufactured to have the highest quality possible. Acushnet Company
4 implements rigorous quality control measures to ensure that its golf ball products are
5 manufactured to meet or exceed high quality standards. For example, there are over 90 quality
6 checks for the Titleist® Pro V1® and 120 quality checks that go into the Titleist® Pro V1x® to
7 ensure that every ball is worthy of bearing the Titleist® brand.

9 9. Acushnet Company devotes significant resources each year on research and
10 development, including in particular on golf ball research and development. Acushnet Company
11 has approximately 80 scientists, chemists, engineers and technicians dedicated to golf ball
12 innovation. This commitment to innovation helps to ensure that Acushnet Company is on the
13 cutting edge of golf ball technology so that it can consistently deliver the highest quality and best
14 performing golf ball products.

16 10. Acushnet Company owns two state-of-the-art testing facilities in Acushnet,
17 Massachusetts and Oceanside, California to conduct robot testing and player testing. At these
18 facilities, Acushnet Company tests and gathers data and feedback to validate new products prior
19 to market launch.

21 11. The Titleist® Pro V1® and Pro V1x® golf balls are covered by a large number of
22 patents owned by Acushnet Company, obtained as a result of Acushnet Company's research and
23 development efforts.

24 12. The Pro V1® ball's spherically-tiled dimple design and three-piece construction
25 provide exceptional distance, superior short game control, and a soft feel. Shortly after
26 introduction of the Pro V1® in 2000, it became the most-used golf ball on the PGA Tour. The
27

1 Pro V1[®] features technology covered by numerous patents owned by Acushnet Company.

2 13. The Pro V1x[®] ball likewise offers superior performance. It uses a spherically-
3 tiled dimple design and a four-piece construction. The Pro V1x[®] also features technology
4 covered by numerous patents owned by Acushnet Company.

5 14. Titleist[®] Pro V1[®] and Pro V1x[®] golf balls are manufactured in the United States.

6 15. Through Acushnet Company's experience, care, and service in producing and
7 providing its golf ball products, including its Titleist[®] Pro V1[®] and Pro V1x[®] golf balls, Acushnet
8 Company's golf ball products have become widely known and have acquired a worldwide
9 reputation for excellence. This reputation for excellence is the result of the high quality of the
10 golf ball products, the unparalleled performance of the golf ball products, the technological
11 innovations (including patented innovations) that are embodied by the golf ball products, and the
12 goodwill Acushnet Company has developed with the purchasers of its golf ball products.
13

14 16. Acushnet Company's golf ball products, including its Titleist[®] Pro V1[®] and Pro
15 V1x[®] golf balls, are considered the leading golf balls in the United States and worldwide. Indeed,
16 the packaging and advertising of Titleist[®] golf balls indicates that they are the "#1 ball in golf."[®]
17 Consumers of golf equipment have come to associate the Titleist[®] brand with Acushnet
18 Company's high standards of quality and performance.
19

20 17. More professional golfers on worldwide professional tours trust their success to
21 Titleist[®] golf balls than any other brand golf ball. For example, from January 1, 2017 through
22 June 29, 2017, Titleist[®] Pro V1[®] and Pro V1x[®] golf balls were used 2,361 times in PGA Tour
23 tournaments, resulting in over \$121M in earnings. The next leading brand was used only 355
24 times, for less than \$23M in earnings. During the same time frame, Titleist[®] Pro V1[®] and Pro
25 V1x[®] golf balls were used 2,602 times in European Tour tournaments (the next leading brand
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1 was used 311 times), 1,542 times in LPGA Tour tournaments (the next leading brand was used
2 151 times), 1,392 times in WEB.COM Tour tournaments (the next leading brand was used 217
3 times), and 751 times in Champions Tour tournaments (the next leading brand was used 102
4 times).

5
6 18. In 2016, Titleist® Pro V1® and Pro V1x® golf balls were used by 81% of the
7 players at the U.S. Men's Amateur Championship, 85% of the players at the U.S. Woman's
8 Amateur Championship, 81% of the players at the NCAA Division I Men's Championship and
9 91% of the players at the NCAA Division I Woman's Championship. Amateur golfers are not
10 allowed to receive compensation for use or endorsement of any brand's equipment and their
11 choice of the Titleist® Pro V1® and Pro V1x® golf balls validates the superior performance and
12 superior quality of these balls.

13
14 19. Titleist® golf balls also account for the highest numbers of sales of golf balls in
15 golf shops both on and off golf courses in the United States. For example, in 2015, Titleist® Pro
16 V1® and Pro V1x® golf ball sales accounted for over two-thirds of the premium performance
17 market segment (golf balls that are designed to maximize total performance across all product
18 attributes, including distance, short game spin and control, feel and durability).

19
20 20. By any meaningful measure, as shown above, the Titleist® brand is the leading
21 national brand of golf balls in the United States. Consumers of golf equipment, professional
22 golfers and those in the golf equipment industry have all come to recognize the Titleist® brand
23 as being the leading national brand.

24 **II. COSTCO'S KIRKLAND SIGNATURE GOLF BALL**

25 21. Upon information and belief, Costco does not own or lease a golf ball
26 manufacturing facility.

22. Upon information and belief, Costco does not own or lease a golf ball testing facility.

23. Upon information and belief, Costco does not employ any scientists, chemists, engineers nor technicians dedicated to golf ball innovation.

24. Upon information and belief, Costco began offering for sale in the United States a golf ball it calls its “Kirkland Signature Golf Ball” in or around October 2016. The Kirkland Signature Golf Ball is illustrated in the picture below:



25. The packaging of the Kirkland Signature Golf Ball indicates that the golf balls are manufactured in Korea.

26. The packaging of the Kirkland Signature Golf Ball indicates that “[e]very Kirkland Signature product is guaranteed to meet or exceed the quality standards of the leading national brands.” Costco refers to this statement as the “Kirkland Signature Guarantee” which was misquoted as “meet or exceed the quality standards of leading national brands” in Costco’s Complaint against Acushnet Holdings Corp. discussed below.

27. The Kirkland Signature Guarantee on the packaging of the Kirkland Signature Golf Ball is likely to communicate to a significant number of consumers a claim that the Kirkland Signature Golf Ball “meet[s] or exceed the quality standards” of Titleist® Pro V1® and Pro V1x® golf balls, *i.e.* the leading national brand of golf balls. Indeed, upon information and belief, the

1 Kirkland Signature Guarantee on the packaging of the Kirkland Signature Golf Ball is intended
2 to indicate such a claim to consumers.

3 28. Upon information and belief, Costco introduced the Kirkland Signature Golf Ball
4 in an effort to draw business away from Acushnet Company, and used its Kirkland Signature
5 Guarantee to convince purchasers and potential purchasers of golf ball products that they should
6 purchase the Kirkland Signature Golf Ball instead of the Titleist® Pro V1® and Pro V1x® golf
7 balls, the leading national brand of golf balls.
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9 29. There are no professional golfers on the PGA Tour, the European Tour, the LGPA
10 Tour, the WEB.COM tour, or the Champions Tour that used the Kirkland Signature Golf Ball in
11 any tournament from January 1, 2017 through June 29, 2017.
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13 **III. ACUSHNET COMPANY'S EXTENSIVE TESTING ILLUSTRATES THAT**
14 **ITS GOLF BALL PRODUCTS ARE SUPERIOR TO THE KIRKLAND**
15 **SIGNATURE GOLF BALL**

16 30. The essence of a good golf ball is one that travels far when hit with a driver or
17 other club from the tee (*i.e.*, it is “long off the tee”), that has high back spin when hit with irons,
18 allowing the ball to stop on the green (*i.e.*, it is “soft around the greens”), and that holds up when
19 struck with a golf club many times (*i.e.*, it is “durable”). The Titleist® Pro V1® and Pro V1x®
20 golf balls have all of these characteristics and are demonstrably superior to the Kirkland Signature
21 Golf Ball, despite Costco’s claim that its ball “meet[s] or exceed[s] the quality standards of the
22 leading national brands.” Indeed, as discussed in greater detail below, Acushnet Company has
23 performed testing that conclusively shows that Titleist® Pro V1® and Pro V1x® golf balls are
24 superior to the Kirkland Signature Golf Ball in performance and durability, and thus that Costco’s
25 Kirkland Signature Guarantee is false with respect to its golf ball products.

26 31. Upon information and belief, Costco did not perform any testing to support its
27

claim that the Kirkland Signature Golf Ball “meet[s] or exceed[s] the quality standards” of the Titleist® Pro V1® and Pro V1x® golf balls, the leading national golf balls, prior to offering the Kirkland Signature Golf Ball to the public.

**IV. THE TITLEIST® PRO V1® AND PRO V1X® GOLF BALLS
PERFORM SIGNIFICANTLY BETTER THAN THE KIRKLAND
SIGNATURE GOLF BALL**

32. A well-recognized measure of performance of a premium golf ball is whether the ball is (1) long off the tee when hit with a driver and (2) soft around the greens when hit with irons, thus increasing scoring opportunities. In the head-to-head robot testing discussed below, the Kirkland Signature Golf Ball was shorter off the tee and had less back spin than the Titleist® Pro V1® and Pro V1x® golf balls. Thus, the Kirkland Signature Golf Ball did not perform as well as the Titleist® Pro V1® and Pro V1x® golf balls.

33. In the Fall of 2016, Acushnet Company tested the performance (*i.e.*, distance and spin) of the Kirkland Signature Golf Ball and the Titleist® Pro V1® and Pro V1x® golf balls, using testing robots and protocols Acushnet Company regularly uses in the ordinary course of its business. The testing was performed by a robot that hit 36 samples of each type of ball with the following golf clubs: a driver at settings to hit the Pro V1 golf ball at speeds of 130 mph, 140 mph, 150 mph (average speeds of recreational players), and 167 mph (the average speed of a PGA Tour player); a 5 iron; an 8 iron; a full wedge; and a half wedge. For each hit with the drivers, the distance the ball traveled through the air (“carry”) and the total distance it traveled after rolling was measured. For each hit with the irons and wedges, the back spin of the ball was measured.

34. **Distance Performance.** The results of the distance tests for the Kirkland Signature Golf Ball and the Titleist® Pro V1® and Pro V1x® golf balls during Acushnet

1 Company's robot testing demonstrated that the Kirkland Signature Golf Ball travelled a shorter
2 distance than both the Titleist® Pro V1® and Pro V1x® golf balls for 130 mph drives; that the
3 Kirkland Signature Golf Ball travelled a shorter distance than both the Titleist® Pro V1® and Pro
4 V1x® golf balls for 140 mph drives; that the Kirkland Signature Golf Ball travelled a shorter
5 distance than both the Titleist® Pro V1® and Pro V1x® golf balls for 150 mph drives; and that the
6 Kirkland Signature Golf Ball travelled a shorter distance than both the Titleist® Pro V1® and Pro
7 V1x® golf balls for 167 mph drives.

9 35. **Back Spin Performance.** The results of the back spin tests for the Kirkland
10 Signature Golf Ball and the Titleist® Pro V1® and Pro V1x® golf balls during Acushnet
11 Company's robot testing demonstrated that the Kirkland Signature Golf Ball had less back spin
12 than both the Titleist® Pro V1® and Pro V1x® golf balls for 5 iron shots; that the Kirkland
13 Signature Golf Ball had less back spin than both the Titleist® Pro V1® and Pro V1x® golf balls
14 for 8 iron shots; that the Kirkland Signature Golf Ball had less back spin than both the Titleist®
15 Pro V1® and Pro V1x® golf balls for full wedge shots; and that the Kirkland Signature Golf Ball
16 had less back spin than both the Titleist® Pro V1® and Pro V1x® golf balls for half wedge shots.
17 The performance testing discussed above illustrates that the Titleist® Pro V1® and Pro V1x® golf
18 balls perform significantly better than the Kirkland Signature Golf Ball. Moreover, the
19 performance testing discussed above establishes that the Kirkland Signature Golf Ball does not
20 "meet or exceed the quality standards" of Titleist® Pro V1® and Pro V1x® golf balls, as Costco
21 claims.
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V. THE TITLEIST® PRO V1® AND PRO V1X® GOLF BALLS ARE SIGNIFICANTLY MORE DURABLE THAN THE KIRKLAND SIGNATURE GOLF BALL

36. One well-recognized measure of durability of a golf ball is whether it remains structurally sound when hit with a golf club many times. In the head-to-head testing discussed below, the Kirkland Signature Golf Ball was far less durable than the Titleist® Pro V1® and Pro V1x® golf balls. Indeed, over half of the Kirkland Signature Golf Balls tested by Acushnet Company cracked or became structurally unsound before the testing could even be concluded.

37. In the Fall of 2016, Acushnet Company tested the durability of the Kirkland Signature Golf Ball and the Titleist® Pro V1® and Pro V1x® golf balls, using a testing protocol Acushnet Company regularly uses in the ordinary course of its business. The testing was performed by a machine that hits each golf ball multiple times and records the coefficient of restitution for each hit. Thirty-six samples of each type of ball (Kirkland Signature, Pro V1®, and Pro V1x®) were tested. After each hit, the coefficient of restitution of the ball was measured in order to detect a failure. If a ball failed, the testing on that ball was concluded and the ball was inspected to determine the cause of the failure.

38. The testing of the Kirkland Signature Golf Ball samples revealed that 50% of the samples failed before the testing was three-quarters complete. According to Acushnet Company's standard durability testing protocol, the testing machine stops a durability test if half of the samples fail. Thus, the testing of Kirkland Signature Golf Ball ceased before the testing was three-quarters complete. Inspection of the failed balls revealed that the first part of the ball to fail in the first failed ball was the inner cover. Of the 18 Kirkland Signature Golf Ball failures, 14 failures were due to defective inner covers and four failures were due to defective cores.

39. The results of the testing of the Titleist® Pro V1® and Pro V1x® golf balls are

1 drastically different. Only two of the 36 Pro V1[®] samples failed. The remaining 34 samples did
2 not fail. None of the Pro V1x[®] samples failed.

3 40. The durability testing discussed above illustrates that the Titleist[®] Pro V1[®] and
4 Pro V1x[®] golf balls are significantly more durable, and thus much more likely to remain intact
5 during a round of golf, than the Kirkland Signature Golf Ball. Indeed, the results are not even
6 close; the Kirkland Signature Golf Ball is of substantially lower quality and durability than the
7 Titleist[®] Pro V1[®] and Pro V1x[®] golf balls. Thus, the durability testing above illustrates that the
8 Kirkland Signature Golf Ball does not “meet or exceed the quality standards” of Titleist[®] Pro
9 V1[®] and Pro V1x[®] golf balls, as Costco claims.

11 **VI. ACUSHNET’S LETTER AND COSTCO’S RESPONSE**

12 41. On December 23, 2016, after Costco began offering its Kirkland Signature Golf
13 Ball for sale in the United States, and after Acushnet Company performed the testing described
14 above, Acushnet Company through its counsel sent a letter to Costco. The letter explained that
15 the Kirkland Signature Ball infringes certain patents owned by Acushnet Company, including
16 the patents asserted in this Complaint below. The letter also provided detailed exemplary claim
17 charts illustrating that the Kirkland Signature Ball infringes the patents. Furthermore, the letter
18 explained that Costco was making false advertising statements with respect to its Kirkland
19 Signature Golf Ball, in particular with respect to the Kirkland Signature Guarantee.

20 42. Costco replied and asked that Acushnet Company wait until April 6, 2017 to allow
21 Costco to respond. Costco also stated in its reply that it would not sell the Kirkland Signature
22 Golf Ball during the period of the requested extension. In the interest of seeking to resolve the
23 dispute without the need for litigation, Acushnet Company complied, and waited for Costco’s
24 response.
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1 43. To Acushnet Company's surprise, on March 17, 2017, Costco filed a complaint
2 in this Court seeking a declaratory judgment of non-infringement and invalidity of patent rights
3 and seeking a declaration of no false advertising. Costco improperly named Acushnet Holdings
4 Corporation ("Acushnet Holdings"), Acushnet Company's parent holding corporation, as the
5 defendant in its complaint. The case was assigned number 2:17-cv-423 ("the '423 Action").
6

7 44. The '423 Action is improper because there is no case or controversy between
8 Costco and Acushnet Holdings, as required for a declaratory judgment action. Acushnet
9 Company, not Acushnet Holdings, sent the letter to Costco accusing it of patent infringement and
10 false advertisement. Moreover, Acushnet Company owns the patents discussed in Acushnet
11 Company's letter to Costco and asserted in this Complaint, as indicated on the face of the patents
12 and in the United States Patent & Trademark Office's assignment records. As such, while
13 Acushnet Holdings separately responded to Costco's complaint, Acushnet Company files this
14 Complaint to resolve the dispute between Costco and Acushnet Company.
15

16 45. Shortly after Costco filed the '423 Action, it indicated that it would resume sales
17 of the Kirkland Signature Golf Ball. Upon information and belief, Costco did in fact resume
18 importation into the United States and sales of the Kirkland Signature Golf Ball.
19

20 **COUNT I: INFRINGEMENT OF THE '638 PATENT**

21 46. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs
22 1 through 45 as if fully set forth herein.

23 47. Acushnet Company is the owner by assignment of United States Patent No.
24 6,994,638 ("the '638 patent"), entitled "Golf Balls Comprising Highly-Neutralized Acid
25 Polymers," which was duly and legally issued by the United States Patent and Trademark Office
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1 to Murali Rajagopalan and Michael J. Sullivan on February 7, 2006, a copy of which is attached
2 hereto as Exhibit A.

3 48. Costco, without authority, has made, used, offered to sell, sold, and/or imported
4 into the United States its Kirkland Signature Golf Balls (“the Accused Products”).

5 49. The Accused Products incorporate or make use of the inventions covered by the
6 ‘638 patent, thereby infringing, literally and/or under the doctrine of equivalents, one or more
7 claims of the ‘638 patent. Hence, Costco has directly infringed, and continues to directly
8 infringe, one or more claims of the ‘638 patent. Costco will continue to infringe the ‘638 patent
9 unless enjoined by this Court.
10

11 50. Each of the Accused Products infringes at least claim 1 of the ‘638 Patent.
12 Specifically, the Accused Products include a core comprising a center and an outer core layer, as
13 shown in the following cross-sectional image:
14



21
22 The center comprises a thermoset polybutadiene rubber composition with a first hardness, and
23 the outer core layer comprises a polymer comprised of an acid group fully-neutralized by an
24 organic acid or a salt of the organic acid having a second hardness. The first hardness is from
25 about 50 Shore A to about 55 Shore D. The Accused Products also include an inner cover layer
26 made of an ionomer and an outer cover layer made of polyurethane.
27

1 51. The Accused Products have a first hardness that is less than the second Shore D
2 hardness by at least about 10 points.

3 52. Costco has had knowledge of the '638 patent at least as of December 23, 2016,
4 and Costco knew at least by that date that its Kirkland Signature Golf Ball infringed the '638
5 patent. By virtue of the claim charts Acushnet Company provided, which included specific
6 measurements where appropriate, Costco also knew by December 23, 2016 exactly how the
7 Kirkland Signature Golf Ball infringed the '638 patent. Despite this knowledge, Costco
8 continued to make, use, offer to sell, sell, and/or import the Kirkland Signature Golf Ball.
9 Costco's intentional infringement is egregious, especially when combined with the Kirkland
10 Signature Guarantee, which appears directed to mislead consumers into incorrectly thinking that
11 the infringing Kirkland Signature Golf Ball meets or exceeds the quality of the Titleist® Pro V1®
12 and Pro V1x® products. Because Costco's infringement has been egregious, and was done with
13 knowledge of the '638 patent, Costco is liable for willful infringement and Acushnet Company
14 is entitled to enhanced damages under 35 U.S.C. § 284.
15

16 53. As a direct result of Costco's infringement of the '638 patent, Acushnet Company
17 has been, is being, and will continue to be, seriously damaged and irreparably harmed unless
18 Costco is enjoined by this Court from the actions complained of herein, and thus Acushnet
19 Company is without an adequate remedy at law.
20

21 54. Acushnet Company is entitled to recover from Costco the damages sustained by
22 Acushnet Company as a result of Costco's wrongful acts in an amount subject to proof at trial.
23

24 **COUNT II: INFRINGEMENT OF THE '593 PATENT**

25 55. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs
26 1 through 54 as if fully set forth herein.
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56. Acushnet Company is the owner by assignment of United States Patent No. 8,025,593 (“the ’593 patent”), entitled “Multi-Layer-Core Golf Ball Having Highly-Neutralized Polymer Outer Core Layer,” which was duly and legally issued by the United States Patent and Trademark Office to Murali Rajagopalan and Michael J. Sullivan on September 27, 2011, a copy of which is attached hereto as Exhibit B.

57. The Accused Products incorporate or make use of the inventions covered by the ’593 patent, thereby infringing, literally and/or under the doctrine of equivalents, one or more claims of the ’593 patent. Hence, Costco has directly infringed, and continues to directly infringe, one or more claims of the ’593 patent. Costco will continue to infringe the ’593 patent unless enjoined by this Court.

58. Each of the Accused Products infringes at least claim 1 of the ’593 patent. Specifically, the Accused Products include an inner core layer, an outer core layer, an inner cover layer, and an outer cover layer, as shown in the following cross-sectional image:



The inner core layer comprises a thermoset rubber composition (for example, a thermoset polybutadiene rubber) having a first surface hardness, the thermoplastic outer core layer is made of a fully-neutralized ionomer having a second surface hardness and an inner surface hardness, the inner cover layer is made of an ionomer, and the outer cover layer is made of polyurethane.

1 59. The Accused Products have a first surface hardness that is less than the second
2 surface hardness by at least 5 Shore C and less than the inner surface hardness by at least 5 Shore
3 C.

4 60. Costco has had knowledge of the '593 patent at least as of December 23, 2016,
5 and Costco knew at least by that date that its Kirkland Signature Golf Ball infringed the '593
6 patent. By virtue of the claim charts Acushnet Company provided, which included specific
7 measurements where appropriate, Costco also knew by December 23, 2016 exactly how the
8 Kirkland Signature Golf Ball infringed the '593 patent. Despite this knowledge, Costco
9 continued to make, use, offer to sell, sell, and/or import the Kirkland Signature Golf Ball.
10 Costco's intentional infringement is egregious, especially when combined with the Kirkland
11 Signature Guarantee, which appears directed to mislead consumers into incorrectly thinking that
12 the infringing Kirkland Signature Golf Ball meets or exceeds the quality of the Titleist® Pro V1®
13 and Pro V1x® products. Because Costco's infringement has been egregious, and was done with
14 knowledge of the '593 patent, Costco is liable for willful infringement and Acushnet Company
15 is entitled to enhanced damages under 35 U.S.C. § 284.
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18 61. As a direct result of Costco's infringement of the '593 patent, Acushnet Company
19 has been, is being, and will continue to be, seriously damaged and irreparably harmed unless
20 Costco is enjoined by this Court from the actions complained of herein, and thus Acushnet
21 Company is without an adequate remedy at law.
22

23 62. Acushnet Company is entitled to recover from Costco the damages sustained by
24 Acushnet Company as a result of Costco's wrongful acts in an amount subject to proof at trial.
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COUNT III: INFRINGEMENT OF THE '632 PATENT

63. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs 1 through 62 as if fully set forth herein.

64. Acushnet Company is the owner by assignment of United States Patent No. 8,123,632 (“the ’632 patent”), entitled “Multi-Layer Golf Ball,” which was duly and legally issued by the United States Patent and Trademark Office to Michael J. Sullivan, Derek A. Ladd, William E. Morgan, and Herbert C. Boehm on February 28, 2012, a copy of which is attached hereto as Exhibit C.

65. The Accused Products incorporate or make use of the inventions covered by the ’632 patent, thereby infringing, literally and/or under the doctrine of equivalents, one or more claims of the ’632 patent. Hence, Costco has directly infringed, and continues to directly infringe, one or more claims of the ’632 patent. Costco will continue to infringe the ’632 patent unless enjoined by this Court.

66. Each of the Accused Products infringes at least claim 17 of the ’632 patent. Specifically, the Accused Products include an inner core layer, an outer core layer, an inner cover layer, and an outer cover layer, as shown in the following cross-sectional image:



1 The inner core layer is formed from a rubber composition (for example, a thermoset
2 polybutadiene rubber) and has a diameter between 1.100 and 1.400 inches, a center hardness of
3 50 Shore C or greater, and an outer surface hardness of 65 Shore C or greater. The inner cover
4 layer is formed from a thermoplastic composition and has a material hardness between 80 Shore
5 C and 95 Shore C. The outer cover layer is formed from a polyurethane composition.

6 67. The outer core layer of the Accused Products is formed from a highly neutralized
7 polymer composition and has an outer surface hardness of 75 Shore C or greater.

8 68. Costco has had knowledge of the '632 patent at least as of December 23, 2016,
9 and Costco knew at least by that date that its Kirkland Signature Golf Ball infringed the '632
10 patent. By virtue of the claim charts Acushnet Company provided, which included specific
11 measurements where appropriate, Costco also knew by December 23, 2016 exactly how the
12 Kirkland Signature Golf Ball infringed the '632 patent. Despite this knowledge, Costco
13 continued to make, use, offer to sell, sell, and/or import the Kirkland Signature Golf Ball.
14 Costco's intentional infringement is egregious, especially when combined with the Kirkland
15 Signature Guarantee, which appears directed to mislead consumers into incorrectly thinking that
16 the infringing Kirkland Signature Golf Ball meets or exceeds the quality of the Titleist® Pro V1®
17 and Pro V1x® products. Because Costco's infringement has been egregious, and was done with
18 knowledge of the '632 patent, Costco is liable for willful infringement and Acushnet Company
19 is entitled to enhanced damages under 35 U.S.C. § 284.
20

21 69. As a direct result of Costco's infringement of the '632 patent, Acushnet Company
22 has been, is being, and will continue to be, seriously damaged and irreparably harmed unless
23 Costco is enjoined by this Court from the actions complained of herein, and thus Acushnet
24 Company is without an adequate remedy at law.
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70. Acushnet Company is entitled to recover from Costco the damages sustained by Acushnet Company as a result of Costco's wrongful acts in an amount subject to proof at trial.

COUNT IV: INFRINGEMENT OF THE '201 PATENT

71. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs 1 through 70 as if fully set forth herein.

72. Acushnet Company is the owner by assignment of United States Patent No. 8,257,201 ("the '201 patent"), entitled "Multi-Layer-Core Golf Ball Having Highly-Neutralized Polymer Outer Core Layer," which was duly and legally issued by the United States Patent and Trademark Office to Murali Rajagopalan and Michael J. Sullivan on September 4, 2012, a copy of which is attached hereto as Exhibit D.

73. The Accused Products incorporate or make use of the inventions covered by the '201 patent, thereby infringing, literally and/or under the doctrine of equivalents, one or more claims of the '201 patent. Hence, Costco has directly infringed, and continues to directly infringe, one or more claims of the '201 patent. Costco will continue to infringe the '201 patent unless enjoined by this Court.

74. Each of the Accused Products infringes at least claim 1 of the '201 patent. Specifically, the Accused Products include an inner core layer, a thermoplastic outer core layer, an inner cover layer, and an outer cover layer, as shown in the following cross-sectional image:



1 The inner core layer comprises a thermoset rubber composition (for example, a thermoset
2 polybutadiene rubber) and has surface hardness. The thermoplastic outer core layer has a surface
3 hardness and an inner surface hardness and comprises a fully neutralized copolymer of ethylene
4 and an $\alpha\beta$ -unsaturated carboxylic acid, an organic acid or salt thereof.

5 75. The Accused Products have a surface hardness of the inner core that is less than
6 the surface hardness of the outer core layer by 3 Shore D or greater and less than the inner surface
7 hardness of the outer core layer by 3 Shore D or greater.

8 76. Costco has had knowledge of the '201 patent at least as of December 23, 2016,
9 and Costco knew at least by that date that its Kirkland Signature Golf Ball infringed the '201
10 patent. By virtue of the claim charts Acushnet Company provided, which included specific
11 measurements where appropriate, Costco also knew by December 23, 2016 exactly how the
12 Kirkland Signature Golf Ball infringed the '201 patent. Despite this knowledge, Costco
13 continued to make, use, offer to sell, sell, and/or import the Kirkland Signature Golf Ball.
14 Costco's intentional infringement is egregious, especially when combined with the Kirkland
15 Signature Guarantee, which appears directed to mislead consumers into incorrectly thinking that
16 the infringing Kirkland Signature Golf Ball meets or exceeds the quality of the Titleist® Pro V1®
17 and Pro V1x® products. Because Costco's infringement has been egregious, and was done with
18 knowledge of the '201 patent, Costco is liable for willful infringement and Acushnet Company
19 is entitled to enhanced damages under 35 U.S.C. § 284.
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21

22 77. As a direct result of Costco's infringement of the '201 patent, Acushnet Company
23 has been, is being, and will continue to be, seriously damaged and irreparably harmed unless
24 Costco is enjoined by this Court from the actions complained of herein, and thus Acushnet
25 Company is without an adequate remedy at law.
26
27

78. Acushnet Company is entitled to recover from Costco the damages sustained by Acushnet Company as a result of Costco's wrongful acts in an amount subject to proof at trial.

COUNT V: INFRINGEMENT OF THE '507 PATENT

79. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs 1 through 78 as if fully set forth herein.

80. Acushnet Company is the owner by assignment of United States Patent No. 8,444,507 ("the '507 patent"), entitled "Multi-Layer Golf Ball," which was duly and legally issued by the United States Patent and Trademark Office to Michael J. Sullivan, Derek A. Ladd, William E. Morgan, and Herbert C. Boehm on May 21, 2013, a copy of which is attached hereto as Exhibit E.

81. The Accused Products incorporate or make use of the inventions covered by the '507 patent, thereby infringing, literally and/or under the doctrine of equivalents, one or more claims of the '507 patent. Hence, Costco has directly infringed, and continues to directly infringe, one or more claims of the '507 patent. Costco will continue to infringe the '507 patent unless enjoined by this Court.

82. Each of the Accused Products infringes at least claim 17 of the '507 patent. Specifically, the Accused Products include an inner core layer, an outer core layer, an inner cover layer, and an outer cover layer, as shown in the following cross-sectional image:



1
2 The inner core layer is formed from a rubber composition (for example, a thermoset
3 polybutadiene rubber) and has a diameter between 0.75 and 1.4 inches, a center hardness of about
4 50 Shore C or greater, and an outer surface hardness of about 65 Shore C or greater. The outer
5 core layer has an outer diameter between 1.4 and about 1.59 inches and is formed from a highly
6 neutralized polymer composition. The inner cover layer is formed from a thermoplastic
7 composition and has a material hardness between about 75 Shore C and about 95 Shore C. The
8 outer cover layer is formed from a polyurethane composition.

9 83. The Accused Products have an outer core having an outer surface hardness of
10 about 75 Shore C or greater.

11 84. Costco has had knowledge of the '507 patent at least as of December 23, 2016,
12 and Costco knew at least by that date that its Kirkland Signature Golf Ball infringed the '507
13 patent. By virtue of the claim charts Acushnet Company provided, which included specific
14 measurements where appropriate, Costco also knew by December 23, 2016 exactly how the
15 Kirkland Signature Golf Ball infringed the '507 patent. Despite this knowledge, Costco
16 continued to make, use, offer to sell, sell, and/or import the Kirkland Signature Golf Ball.
17 Costco's intentional infringement is egregious, especially when combined with the Kirkland
18 Signature Guarantee, which appears directed to mislead consumers into incorrectly thinking that
19 the infringing Kirkland Signature Golf Ball meets or exceeds the quality of the Titleist® Pro V1®
20 and Pro V1x® products. Because Costco's infringement has been egregious, and was done with
21 knowledge of the '507 patent, Costco is liable for willful infringement and Acushnet Company
22 is entitled to enhanced damages under 35 U.S.C. § 284.

23 85. As a direct result of Costco's infringement of the '507 patent, Acushnet Company
24 has been, is being, and will continue to be, seriously damaged and irreparably harmed unless
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1 Costco is enjoined by this Court from the actions complained of herein, and thus Acushnet
2 Company is without an adequate remedy at law.

3 86. Acushnet Company is entitled to recover from Costco the damages sustained by
4 Acushnet Company as a result of Costco's wrongful acts in an amount subject to proof at trial.

5
6 **COUNT VI: INFRINGEMENT OF THE '944 PATENT**

7 87. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs
8 1 through 86 as if fully set forth herein.

9 88. Acushnet Company is the owner by assignment of United States Patent No.
10 9,320,944 ("the '944 patent"), entitled "Multi-Layer Cover Dual Core Golf Ball Having a High
11 Acid Casing and Low Gradient Center," which was duly and legally issued by the United States
12 Patent and Trademark Office to Michael J. Sullivan, Brian Comeau, Scott Cooper, Douglas E.
13 Jones, and Derek A. Ladd on April 26, 2016, a copy of which is attached hereto as Exhibit F.

14 89. The Accused Products incorporate or make use of the inventions covered by the
15 '944 patent, thereby infringing, literally and/or under the doctrine of equivalents, one or more
16 claims of the '944 patent. Hence, Costco has directly infringed, and continues to directly
17 infringe, one or more claims of the '944 patent. Costco will continue to infringe the '944 patent
18 unless enjoined by this Court.

19 90. Each of the Accused Products infringes at least claim 1 of the '944 patent.
20 Specifically, the Accused Products include an inner core layer, an outer core layer disposed about
21 the inner core layer to form a dual core, an inner cover layer disposed about the dual core, and
22 an outer cover layer disposed about the inner cover layer, as shown in the following cross-
23 sectional image:
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The inner core layer has an outer surface and a geometric center, is formed from a substantially homogenous rubber composition, and has an inner core surface hardness greater than the geometric center hardness by about 1 to 10 Shore C to define a shallow positive hardness gradient. The inner cover layer is a high-acid ionomer blend having an acid content of about 16% or greater and has a material hardness of between about 66 and 75 Shore D. The outer cover layer is comprised of polyurethane and has a material hardness between about 38 Shore D and 56 Shore D.

91. The Accused Products have a dual core surface hardness that is at least about 85 Shore C.

92. Costco has had knowledge of the '944 patent at least as of December 23, 2016, and Costco knew at least by that date that its Kirkland Signature Golf Ball infringed the '944 patent. By virtue of the claim charts Acushnet Company provided, which included specific measurements where appropriate, Costco also knew by December 23, 2016 exactly how the Kirkland Signature Golf Ball infringed the '944 patent. Despite this knowledge, Costco continued to make, use, offer to sell, sell, and/or import the Kirkland Signature Golf Ball. Costco's intentional infringement is egregious, especially when combined with the Kirkland Signature Guarantee, which appears directed to mislead consumers into incorrectly thinking that the infringing Kirkland Signature Golf Ball meets or exceeds the quality of the Titleist® Pro V1®

1 and Pro V1x[®] products. Because Costco's infringement has been egregious, and was done with
2 knowledge of the '944 patent, Costco is liable for willful infringement and Acushnet Company
3 is entitled to enhanced damages under 35 U.S.C. § 284.

4 93. As a direct result of Costco's infringement of the '944 patent, Acushnet Company
5 has been, is being, and will continue to be, seriously damaged and irreparably harmed unless
6 Costco is enjoined by this Court from the actions complained of herein, and thus Acushnet
7 Company is without an adequate remedy at law.

9 94. Acushnet Company is entitled to recover from Costco the damages sustained by
10 Acushnet Company as a result of Costco's wrongful acts in an amount subject to proof at trial.

11 **COUNT VII: INFRINGEMENT OF THE '161 PATENT**

12 95. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs
13 1 through 94 as if fully set forth herein.

14 96. Acushnet Company is the owner by assignment of United States Patent No.
15 6,358,161 ("the '161 patent"), entitled "Golf Ball Dimple Pattern," which was duly and legally
16 issued by the United States Patent and Trademark Office to Steven Aoyama on March 19, 2002,
17 a copy of which is attached hereto as Exhibit G.

18 97. The Accused Products incorporate or make use of the inventions covered by the
19 '161 patent, thereby infringing, literally and/or under the doctrine of equivalents, one or more
20 claims of the '161 patent. Hence, Costco has directly infringed, and continues to directly
21 infringe, one or more claims of the '161 patent. Costco will continue to infringe the '161 patent
22 unless enjoined by this Court.

23 98. Each of the Accused Products infringes at least claim 7 of the '161 patent.
24 Specifically, the Accused Products include an outside surface with a plurality of round dimples
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1 having at least three different dimple diameters. The total number of dimples on the outside
2 surface is between about 350 and about 450. About 80% of the dimples have a diameter of about
3 0.11 inches or greater. The dimples have spaces between adjacent dimples, and less than 30%
4 of the spaces are greater than 0.01 inches.

5 99. The dimples of the Accused Products cover more than 80% of the outer surface.

6 100. Costco has had knowledge of the '161 patent at least as of December 23, 2016,
7 and Costco knew at least by that date that its Kirkland Signature Golf Ball infringed the '161
8 patent. By virtue of the claim charts Acushnet Company provided, which included specific
9 measurements where appropriate, Costco also knew by December 23, 2016 exactly how the
10 Kirkland Signature Golf Ball infringed the '161 patent. Despite this knowledge, Costco
11 continued to make, use, offer to sell, sell, and/or import the Kirkland Signature Golf Ball.
12 Costco's intentional infringement is egregious, especially when combined with the Kirkland
13 Signature Guarantee, which appears directed to mislead consumers into incorrectly thinking that
14 the infringing Kirkland Signature Golf Ball meets or exceeds the quality of the Titleist® Pro V1®
15 and Pro V1x® products. Because Costco's infringement has been egregious, and was done with
16 knowledge of the '161 patent, Costco is liable for willful infringement and Acushnet Company
17 is entitled to enhanced damages under 35 U.S.C. § 284.
18

19 101. As a direct result of Costco's infringement of the '161 patent, Acushnet Company
20 has been, is being, and will continue to be, seriously damaged and irreparably harmed unless
21 Costco is enjoined by this Court from the actions complained of herein, and thus Acushnet
22 Company is without an adequate remedy at law.

23 102. Acushnet Company is entitled to recover from Costco the damages sustained by
24 Acushnet Company as a result of Costco's wrongful acts in an amount subject to proof at trial.
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COUNT VIII: INFRINGEMENT OF THE '472 PATENT

103. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs 1 through 102 as if fully set forth herein.

104. Acushnet Company is the owner by assignment of United States Patent No. 7,163,472 (“the ’472 patent”), entitled “Golf Ball Dimples with a Catenary Curve Profile,” which was duly and legally issued by the United States Patent and Trademark Office to Jeffrey L. Dalton and Laurent Bissonnette on January 16, 2007, a copy of which is attached hereto as Exhibit H.

105. The Accused Products incorporate or make use of the inventions covered by the ’472 patent, thereby infringing, literally and/or under the doctrine of equivalents, one or more claims of the ’472 patent. Hence, Costco has directly infringed, and continues to directly infringe, one or more claims of the ’472 patent. Costco will continue to infringe the ’472 patent unless enjoined by this Court.

106. Each of the Accused Products infringes at least claim 5 of the ’472 patent. Specifically, the Accused Products have a core and a cover, and have a lift coefficient between 0.09 and 0.27 at a Reynolds number of 222,727 and spin ratio of 0.088. As illustrated in the picture below, the cover has a plurality of recessed dimples on the surface thereof:



107. At least one dimple on the cover of the Accused Products is defined by the revolution of a Catenary curve.

108. Costco has had knowledge of the '472 patent at least as of December 23, 2016, and Costco knew at least by that date that its Kirkland Signature Golf Ball infringed the '472 patent. By virtue of the claim charts Acushnet Company provided, which included specific measurements where appropriate, Costco also knew by December 23, 2016 exactly how the Kirkland Signature Golf Ball infringed the '472 patent. Despite this knowledge, Costco continued to make, use, offer to sell, sell, and/or import the Kirkland Signature Golf Ball. Costco's intentional infringement is egregious, especially when combined with the Kirkland Signature Guarantee, which appears directed to mislead consumers into incorrectly thinking that the infringing Kirkland Signature Golf Ball meets or exceeds the quality of the Titleist® Pro V1® and Pro V1x® products. Because Costco's infringement has been egregious, and was done with knowledge of the '472 patent, Costco is liable for willful infringement and Acushnet Company is entitled to enhanced damages under 35 U.S.C. § 284.

109. As a direct result of Costco's infringement of the '472 patent, Acushnet Company has been, is being, and will continue to be, seriously damaged and irreparably harmed unless Costco is enjoined by this Court from the actions complained of herein, and thus Acushnet Company is without an adequate remedy at law.

110. Acushnet Company is entitled to recover from Costco the damages sustained by Acushnet Company as a result of Costco's wrongful acts in an amount subject to proof at trial.

COUNT IX: INFRINGEMENT OF THE '439 PATENT

111. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs 1 through 110 as if fully set forth herein.

112. Acushnet Company is the owner by assignment of United States Patent No. 7,887,439 ("the '439 patent"), entitled "Golf Ball Dimples with a Catenary Curve Profile," which was duly and legally issued by the United States Patent and Trademark Office to Steven Aoyama, Nicholas M. Nardacci, Jeffrey L. Dalton, and Laurent Bissonnette on February 15, 2011, a copy of which is attached hereto as Exhibit I.

113. Acushnet Company filed a petition to correct the inventorship of the '439 patent, requesting that the U.S.P.T.O. name Jeffrey L. Dalton and Laurent Bissonnette as inventors. That petition was granted by the U.S.P.T.O.

114. The Accused Products incorporate or make use of the inventions covered by the '439 patent, thereby infringing, literally and/or under the doctrine of equivalents, one or more claims of the '439 patent. Hence, Costco has directly infringed, and continues to directly infringe, one or more claims of the '439 patent. Costco will continue to infringe the '439 patent unless enjoined by this Court.

115. Each of the Accused Products infringes at least claim 1 of the '439 patent. Specifically, as illustrated in the picture below, each of the Accused Products have a plurality of recessed dimples on the surface thereof:



116. At least a portion of the plurality of the recessed dimples on the Accused Products have a profile defined by the revolution of a Catenary curve according to the following function:

$$y = \frac{d_c(\cosh sf * x) - 1}{\cosh\left(sf * \frac{D}{2}\right) - 1}$$

wherein y is the vertical direction coordinate away from the center of the ball with 0 at the center of the dimple; x is the horizontal (radial) direction coordinate from the dimple apex to the dimple surface with 0 at the center of the dimple; sf is a shape factor; d_c is the chordal depth of the dimple; and D is the diameter of the dimple.

117. Costco has had knowledge of the '439 patent at least as of December 23, 2016, and Costco knew at least by that date that its Kirkland Signature Golf Ball infringed the '439 patent. By virtue of the claim charts Acushnet Company provided, which included specific measurements where appropriate, Costco also knew by December 23, 2016 exactly how the Kirkland Signature Golf Ball infringed the '439 patent. Despite this knowledge, Costco continued to make, use, offer to sell, sell, and/or import the Kirkland Signature Golf Ball.

1 Costco's intentional infringement is egregious, especially when combined with the Kirkland
2 Signature Guarantee, which appears directed to mislead consumers into incorrectly thinking that
3 the infringing Kirkland Signature Golf Ball meets or exceeds the quality of the Titleist® Pro V1®
4 and Pro V1x® products. Because Costco's infringement has been egregious, and was done with
5 knowledge of the '439 patent, Costco is liable for willful infringement and Acushnet Company
6 is entitled to enhanced damages under 35 U.S.C. § 284.
7

8 118. As a direct result of Costco's infringement of the '439 patent, Acushnet Company
9 has been, is being, and will continue to be, seriously damaged and irreparably harmed unless
10 Costco is enjoined by this Court from the actions complained of herein, and thus Acushnet
11 Company is without an adequate remedy at law.

12 119. Acushnet Company is entitled to recover from Costco the damages sustained by
13 Acushnet Company as a result of Costco's wrongful acts in an amount subject to proof at trial.
14

15 **COUNT X: INFRINGEMENT OF THE '572 PATENT**

16 120. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs
17 1 through 119 as if fully set forth herein.

18 121. Acushnet Company is the owner by assignment of United States Patent No.
19 7,641,572 ("the '572 patent"), entitled "Golf Ball Dimples with a Catenary Curve Profile," which
20 was duly and legally issued by the United States Patent and Trademark Office to Steven Aoyama,
21 Nicholas M. Nardacci, Jeffrey L. Dalton, and Laurent Bissonnette on January 5, 2010, a copy of
22 which is attached hereto as Exhibit J.
23

24 122. Acushnet Company filed a petition to correct the inventorship of the '572 patent,
25 requesting that the U.S.P.T.O. name Jeffrey L. Dalton and Laurent Bissonnette as inventors. That
26 petition was granted by the U.S.P.T.O.
27

123. The Accused Products incorporate or make use of the inventions covered by the '572 patent, thereby infringing, literally and/or under the doctrine of equivalents, one or more claims of the '572 patent. Hence, Costco has directly infringed, and continues to directly infringe, one or more claims of the '572 patent. Costco will continue to infringe the '572 patent unless enjoined by this Court.

124. Each of the Accused Products infringes at least claim 1 of the '572 patent. Specifically, as illustrated in the picture below, each of the Accused Products have a plurality of recessed dimples on the surface thereof:



125. At least a portion of the plurality of the recessed dimples on the Accused Products have a profile defined by the revolution of a Catenary curve according to the following function:

$$y = \frac{d_c(\cosh sf * x) - 1}{\cosh\left(sf * \frac{D}{2}\right) - 1}$$

wherein y is the vertical direction coordinate away from the center of the ball with 0 at the center of the dimple; x is the horizontal (radial) direction coordinate from the dimple apex to the dimple surface with 0 at the center of the dimple; sf is a shape factor; d_c is the chordal depth of the dimple; and D is the diameter of the dimple. The dimple diameter of the balls is between about

1 0.115 inches and about 0.185 inches, the shape factor is between about 5 and about 200, and the
2 chordal depth is between about 0.002 inches and 0.008 inches.

3 126. Costco has had knowledge of the '572 patent at least as of December 23, 2016,
4 and Costco knew at least by that date that its Kirkland Signature Golf Ball infringed the '572
5 patent. By virtue of the claim charts Acushnet Company provided, which included specific
6 measurements where appropriate, Costco also knew by December 23, 2016 exactly how the
7 Kirkland Signature Golf Ball infringed the '572 patent. Despite this knowledge, Costco
8 continued to make, use, offer to sell, sell, and/or import the Kirkland Signature Golf Ball.
9 Costco's intentional infringement is egregious, especially when combined with the Kirkland
10 Signature Guarantee, which appears directed to mislead consumers into incorrectly thinking that
11 the infringing Kirkland Signature Golf Ball meets or exceeds the quality of the Titleist® Pro V1®
12 and Pro V1x® products. Because Costco's infringement has been egregious, and was done with
13 knowledge of the '572 patent, Costco is liable for willful infringement and Acushnet Company
14 is entitled to enhanced damages under 35 U.S.C. § 284.
15
16

17 127. As a direct result of Costco's infringement of the '572 patent, Acushnet Company
18 has been, is being, and will continue to be, seriously damaged and irreparably harmed unless
19 Costco is enjoined by this Court from the actions complained of herein, and thus Acushnet
20 Company is without an adequate remedy at law.
21

22 128. Acushnet Company is entitled to recover from Costco the damages sustained by
23 Acushnet Company as a result of Costco's wrongful acts in an amount subject to proof at trial.

24 **COUNT XI: FALSE ADVERTISING (VIOLATION OF THE LANHAM ACT)**

25 129. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs
26 1 through 128 as if fully set forth herein.
27

1 130. The packaging of the Kirkland Signature Golf Ball includes the “Kirkland
2 Signature Guarantee” that claims that “[e]very Kirkland Signature product is guaranteed to meet
3 or exceed the quality standards of the leading national brands.”

4 131. As shown above, Acushnet Company’s testing demonstrates conclusively that the
5 Kirkland Signature Guarantee is false because the quality of the Kirkland Signature Golf Ball
6 does not meet or exceed the quality of Acushnet Company’s leading national brand golf ball
7 products, including Acushnet Company’s Titleist® Pro V1® and Pro V1x® golf balls. Indeed, the
8 performance and durability of the Kirkland Signature Golf Ball is significantly lower than that
9 of Acushnet Company’s Titleist® Pro V1® and Pro V1x® golf balls. Thus, Costco’s Kirkland
10 Signature Guarantee is false and misleading.

11 132. Upon information and belief, Costco has not performed any testing or other
12 studies comparing the Kirkland Signature Golf Ball to Acushnet Company’s leading national
13 brand golf ball products, including Acushnet Company’s Titleist® Pro V1® and Pro V1x® golf
14 balls. Thus, Costco has no reasonable basis to make its Kirkland Signature Guarantee.

15 133. Upon information and belief, Costco does not have or know of any robot testing
16 comparing the Kirkland Signature Golf Ball to Acushnet Company’s leading national brand golf
17 ball products, including Acushnet Company’s Titleist® Pro V1® and Pro V1x® golf balls, other
18 than Acushnet Company’s tests discussed above. Thus, Costco has no reasonable basis to make
19 its Kirkland Signature Guarantee.

20 134. Costco’s Kirkland Signature Guarantee is used in commercial advertisements
21 and/or promotions in interstate commerce. For example, the statement is included on the
22 packaging of the Kirkland Signature Golf Ball sold by Costco in multiple states within the United
23 States.

1 135. Costco's Kirkland Signature Guarantee is likely to mislead, confuse, and/or
2 deceive a significant number of purchasers and potential purchasers of golf ball products. In
3 particular, Costco's Kirkland Signature Guarantee is likely to deceive such people in a material
4 way, in that it is likely to influence the purchasing decisions of a significant number of purchasers
5 and potential purchasers of golf ball products. For example, Costco's Kirkland Signature
6 Guarantee is likely to deceive a significant number of purchasers and potential purchasers of golf
7 ball products into believing that the Kirkland Signature Golf Ball "meets or exceeds the quality
8 standards" of Acushnet Company's golf ball products, including Acushnet Company's Titleist®
9 Pro V1® and Pro V1x® golf balls.
10

11 136. Costco's Kirkland Signature Guarantee is likely to cause competitive or
12 commercial injury to Acushnet Company. For example, as a result of Costco's Kirkland
13 Signature Guarantee, a significant number of purchasers and potential purchasers of golf ball
14 products will be deceived into believing that the Kirkland Signature Golf Ball is equivalent to
15 the Titleist® Pro V1® and Pro V1x® golf balls. Thus, as a result of Costco's Kirkland Signature
16 Guarantee, Acushnet Company is likely to suffer irreparable damage to its business reputation
17 and goodwill associated with Acushnet Company's products. This damage to Acushnet
18 Company's business reputation and the goodwill associated with the industry leading quality of
19 the Titleist® Pro V1® and Pro V1x® golf balls directly flows from Costco's Kirkland Signature
20 Guarantee.
21
22

23 137. Costco's actions described above constitute false or misleading descriptions of
24 fact, and/or false or misleading representations of fact in commercial advertising or promotion,
25 which are likely to cause confusion, mistake and deception, in violation of Section 43(a) of the
26 Lanham Act, 15 U.S.C. § 1125(a).
27

1 138. Costco's actions described above were performed with reckless disregard for the
2 false and misleading nature of its Kirkland Signature Guarantee and its impact on the public and
3 Acushnet Company, making this an exceptional case pursuant to 15 U.S.C. § 1117.

4 139. Costco's actions described above, unless restrained, will cause, and continue to
5 cause, great and irreparable injury to Acushnet Company in an amount that cannot presently be
6 ascertained, leaving Acushnet Company with no adequate remedy at law.

7 140. Acushnet Company has standing to bring this claim against Costco because, as
8 set forth below, Acushnet Company is likely to suffer an injury to a commercial interest in sales
9 or business reputation proximately caused by Costco's misrepresentations. *See Lexmark Int'l,*
10 *Inc. v. Static Control Components, Inc.*, 134 S. Ct. 1377 (2014).

11
12 **COUNT XII: VIOLATION OF WASHINGTON STATE**
13 **CONSUMER PROTECTION ACT**

14 141. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs
15 1 through 140 as if fully set forth herein.

16 142. The state of Washington has an important interest in ensuring that domestic
17 corporations doing business with Washington residents fully comply with Washington laws.

18 143. As described above, Costco's Kirkland Signature Guarantee is an unfair act or
19 practice that has the capacity to, and does in fact, deceive purchasers and potential purchasers of
20 golf ball products into believing that the Kirkland Signature Golf Ball "meets or exceeds the
21 quality standards" of Acushnet Company's golf ball products, including Acushnet Company's
22 Titleist® Pro V1® and Pro V1x® golf balls.

23 144. Costco's conduct occurred in the conduct of trade or commerce or the sale of
24 products in the state of Washington.

25 145. Costco's unfair and deceptive acts and practices implicate the public interest

1 because they are deceiving or have a tendency or capacity to deceive the consuming public.

2 146. Costco has engaged and continues to engage in the activities alleged herein
3 knowingly, willingly, and deliberately.

4 147. Acushnet Company has been directly and proximately injured in its business and
5 property by Costco's unfair and deceptive acts and practices, in violation of Acushnet Company's
6 rights under RCW § 19.86.020.

8 148. Costco's actions described above have caused and, unless restrained, will
9 continue to cause, great and irreparable injury to Acushnet Company in an amount that cannot
10 presently be ascertained, leaving Acushnet Company with no adequate remedy at law.

11 149. Pursuant to RCW § 19.86.090, Acushnet Company is entitled to actual damages
12 sustained as a result of Costco's actions, treble damages up to the maximum amount permitted
13 by law, attorneys' fees, and statutory costs permitted under RCW § 4.84.010.

15 **COUNT XIII: COMMON LAW UNFAIR COMPETITION**

16 150. Acushnet Company repeats and re-alleges the allegations set forth in Paragraphs
17 1 through 149 as if fully set forth herein.

18 151. As described above, Costco has used and continues to use, in advertising and
19 commerce, false and misleading descriptions of fact, or false and misleading representations of
20 fact, concerning its Kirkland Signature Golf Ball that are material to the purchasing decisions of
21 prospective purchasers. These activities constitute false advertising and unfair competition.

22 152. Costco has engaged in unfair competition willfully and with a bad faith intent to
23 injure Acushnet Company.

25 153. Acushnet Company has sustained, and will continue to sustain, substantial
26 injuries, loss, and damage to its business by reason of the unfair competition of Costco.

1 154. Costco's actions described above have caused and, unless restrained, will
2 continue to cause, great and irreparable injury to Acushnet Company in an amount that cannot
3 presently be ascertained, leaving Acushnet Company with no adequate remedy at law.

4 155. Acushnet Company is entitled to exemplary and punitive damages by reason of
5 Costco's willful, reckless, deliberate and intentional conduct.
6

7 **PRAYER FOR RELIEF**

8 WHEREFORE, Acushnet Company prays for judgment and relief as follows:

9 A. That this Court enter an Order declaring that Costco infringes the '638, '593, '632,
10 '201, '507, '944, '161, '472, '439, and '572 patents;

11 B. That this Court permanently enjoin Costco, its officers, agents, employees,
12 representatives, successors and assigns, and any others acting in concert with it, from infringing
13 the '638, '593, '632, '201, '507, '944, '161, '472, '439, and '572 patents;
14

15 C. That this Court award Acushnet Company adequate damages resulting from
16 Costco's infringement of the '638, '593, '632, '201, '507, '944, '161, '472, '439, and '572
17 patents;

18 D. That this Court award Acushnet Company treble its damages due to Costco's
19 willful infringement of the '638, '593, '632, '201, '507, '944, '161, '472, '439, and '572 patents;

20 E. That this Court declare this to be an exceptional case within the meaning of 35
21 U.S.C. § 285;
22

23 F. That this Court permanently enjoin Costco, its officers, agents, employees,
24 representatives, successors and assigns, and any others acting in concert with it, from making
25 false and misleading representations or any other thing calculated or likely to cause confusion or
26 mistake in the mind of the purchasers or potential purchasers of golf ball products into believing
27

1 that the quality of Costco's golf ball products meet or exceed the quality standards of Acushnet
2 Company's Titleist® Pro V1® and Pro V1x® golf balls;

3 G. That this Court direct Costco to account to Acushnet Company for its profits and
4 order that Acushnet Company recover Costco's illicit profits and damages arising out of the acts
5 of deception described above, and a sum equal to three times such profits or damages (whichever
6 is greater), pursuant to 15 U.S.C. § 1117;

7
8 H. That this Court award Acushnet Company punitive damages in an amount to be
9 determined;

10 I. That this Court award Acushnet Company its costs in this action, together with
11 reasonable attorneys' fees and pre-judgment interest; and

12 J. That this Court grant Acushnet Company such other relief as it deems just and
13 proper.
14

15 **JURY DEMAND**

16 Acushnet Company demands a trial by jury on all issues so triable.

17 Dated: August 10, 2017

18 Respectfully submitted,

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Exhibit A

(12) **United States Patent**
Rajagopalan et al.

(10) **Patent No.:** **US 6,994,638 B2**

(45) **Date of Patent:** ***Feb. 7, 2006**

(54) **GOLF BALLS COMPRISING
HIGHLY-NEUTRALIZED ACID POLYMERS**

(75) Inventors: **Murali Rajagopalan**, South Dartmouth,
MA (US); **Michael J. Sullivan**,
Barrington, RI (US)

(73) Assignee: **Acushnet Company**, Fairhaven, MA
(US)

(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 14 days.

This patent is subject to a terminal dis-
claimer.

(21) Appl. No.: **10/839,595**

(22) Filed: **May 5, 2004**

(65) **Prior Publication Data**

US 2004/0209705 A1 Oct. 21, 2004

Related U.S. Application Data

(63) Continuation of application No. 10/360,238, filed on
Feb. 6, 2003, now Pat. No. 6,824,477, which is a
continuation-in-part of application No. 10/118,719,
filed on Apr. 9, 2002, now Pat. No. 6,756,436.

(60) Provisional application No. 60/301,046, filed on Jun.
26, 2001.

(51) **Int. Cl.**
A63B 37/06 (2006.01)

(52) **U.S. Cl.** **473/377**

(58) **Field of Classification Search** **473/351,**
473/376, 377

See application file for complete search history.

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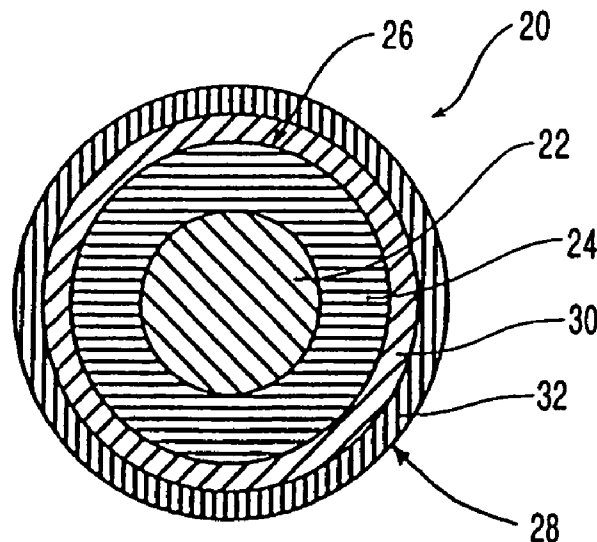
Primary Examiner—Racann Gorden

(74) *Attorney, Agent, or Firm*—William B. Lacy

(57) **ABSTRACT**

A golf ball comprising a core comprised of a polymer containing an acid group fully-neutralized by an organic acid or a salt, a cation source, or a suitable base thereof, the core having a first Shore D hardness, a compression of no greater than about 90, and a diameter of between about 1.00 inches and about 1.64 inches; and a cover layer comprising ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, thermoplastic elastomers, polybutadiene rubber, balata, grafted metallocene-catalyzed polymers, non-grafted metallocene-catalyzed polymers, single-site polymers, high-crystalline acid polymers and their ionomers, or cationic ionomers.

16 Claims, 8 Drawing Sheets



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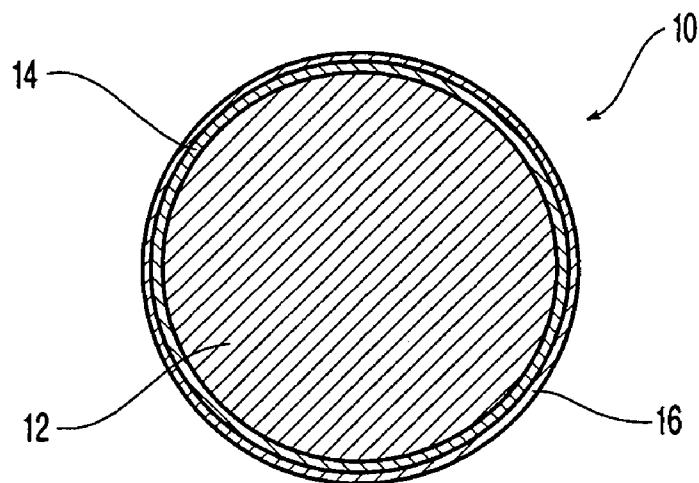


Fig. 1

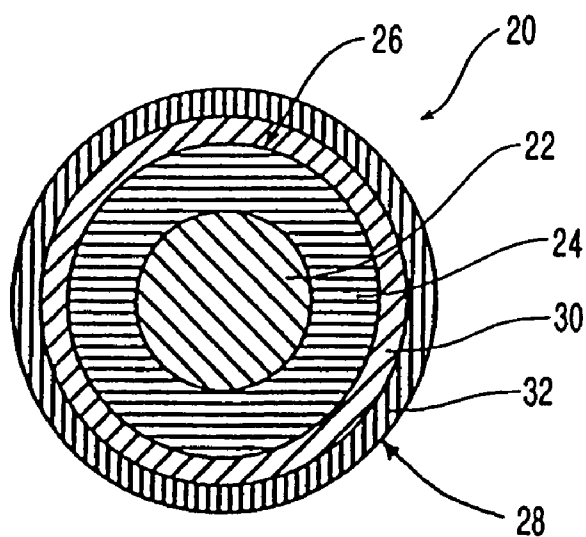


Fig. 2

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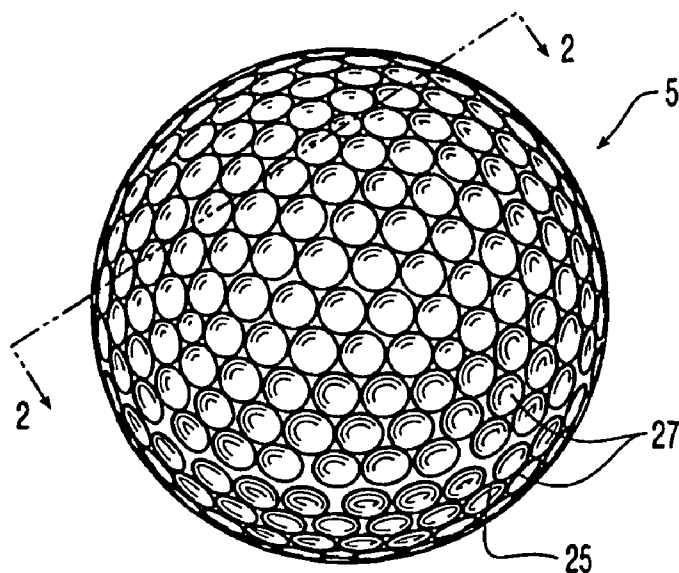


Fig. 3

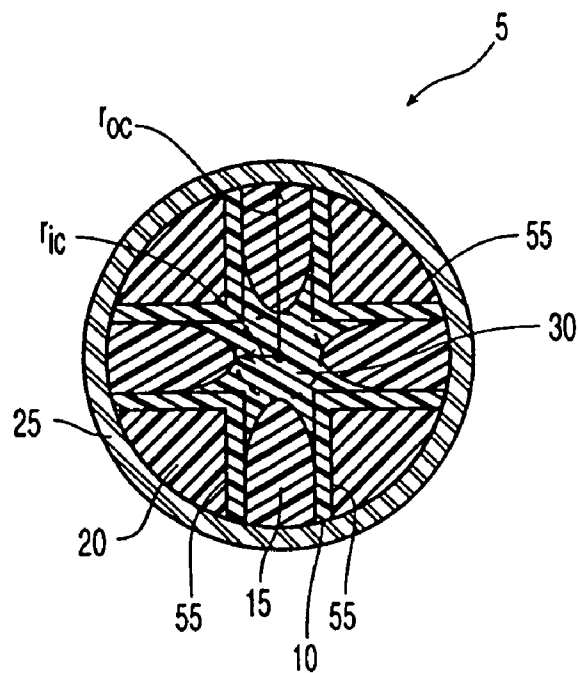


Fig. 4

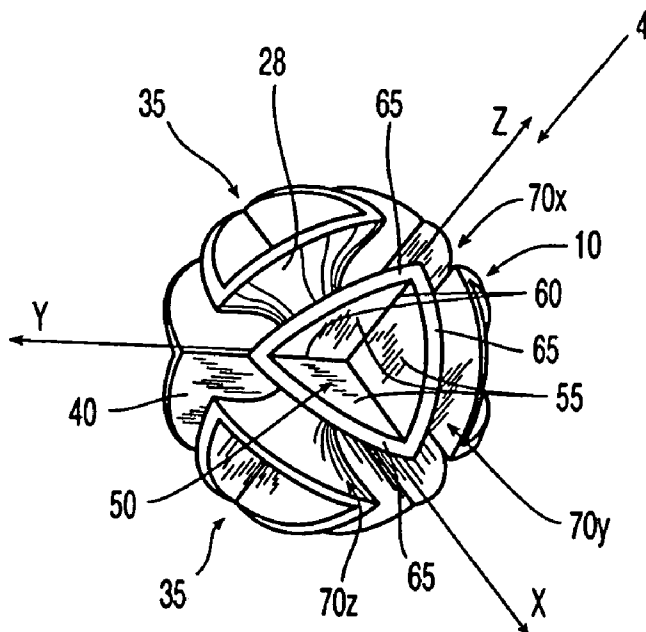


Fig. 5

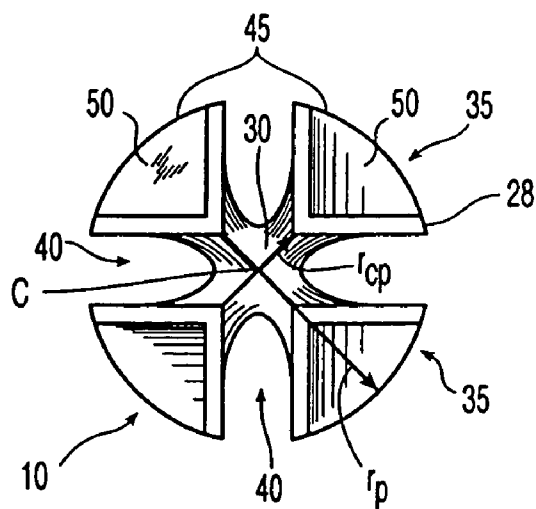


Fig. 6

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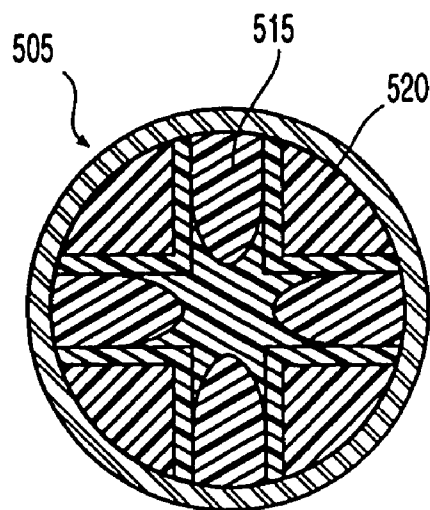


Fig. 7

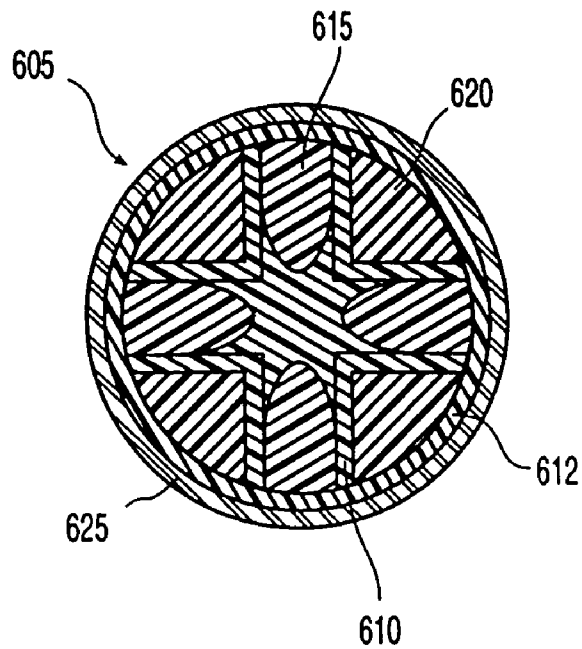


Fig. 8

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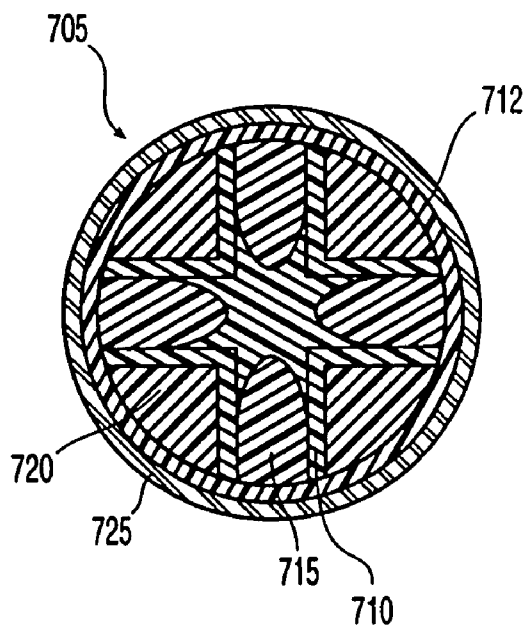


Fig. 9

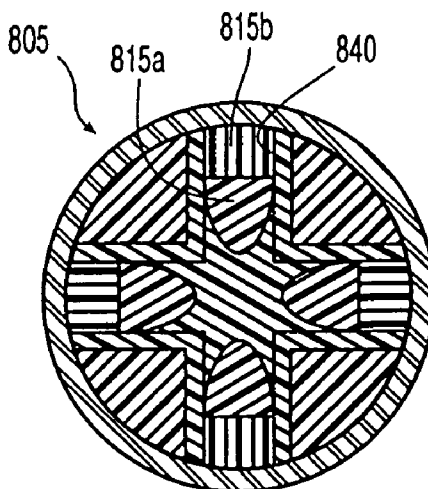


Fig. 10

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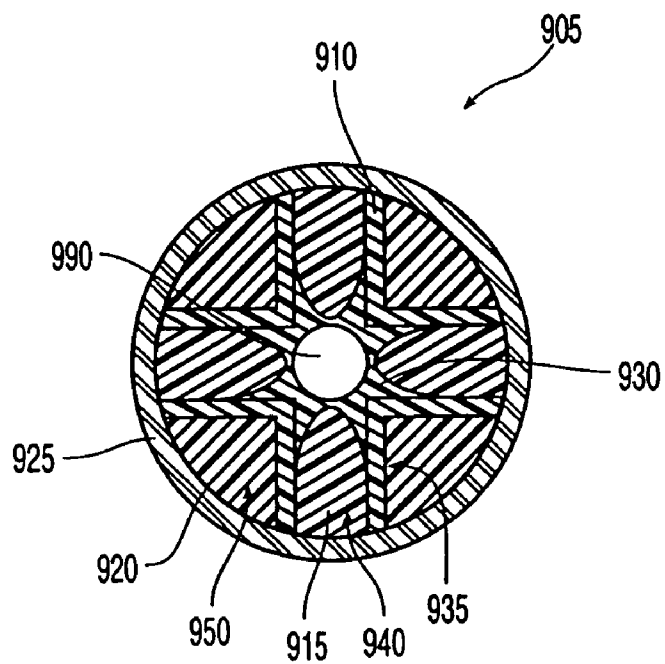


Fig. 11

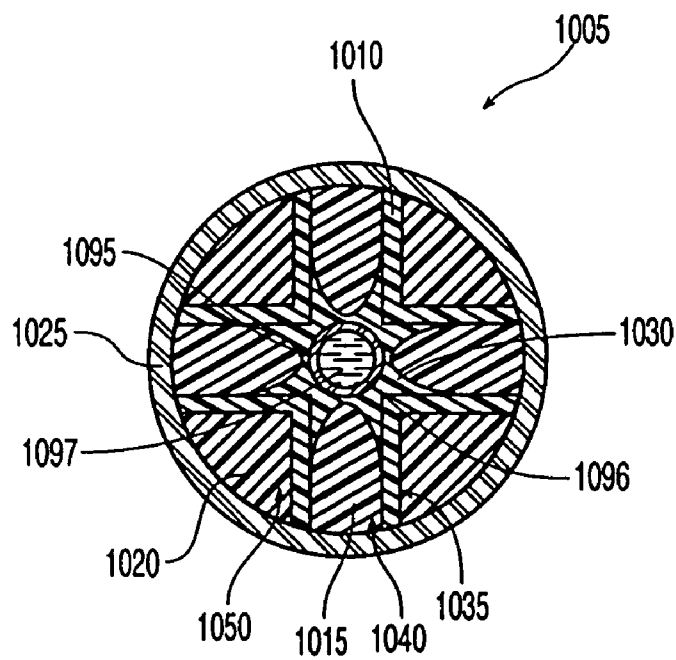


Fig. 12

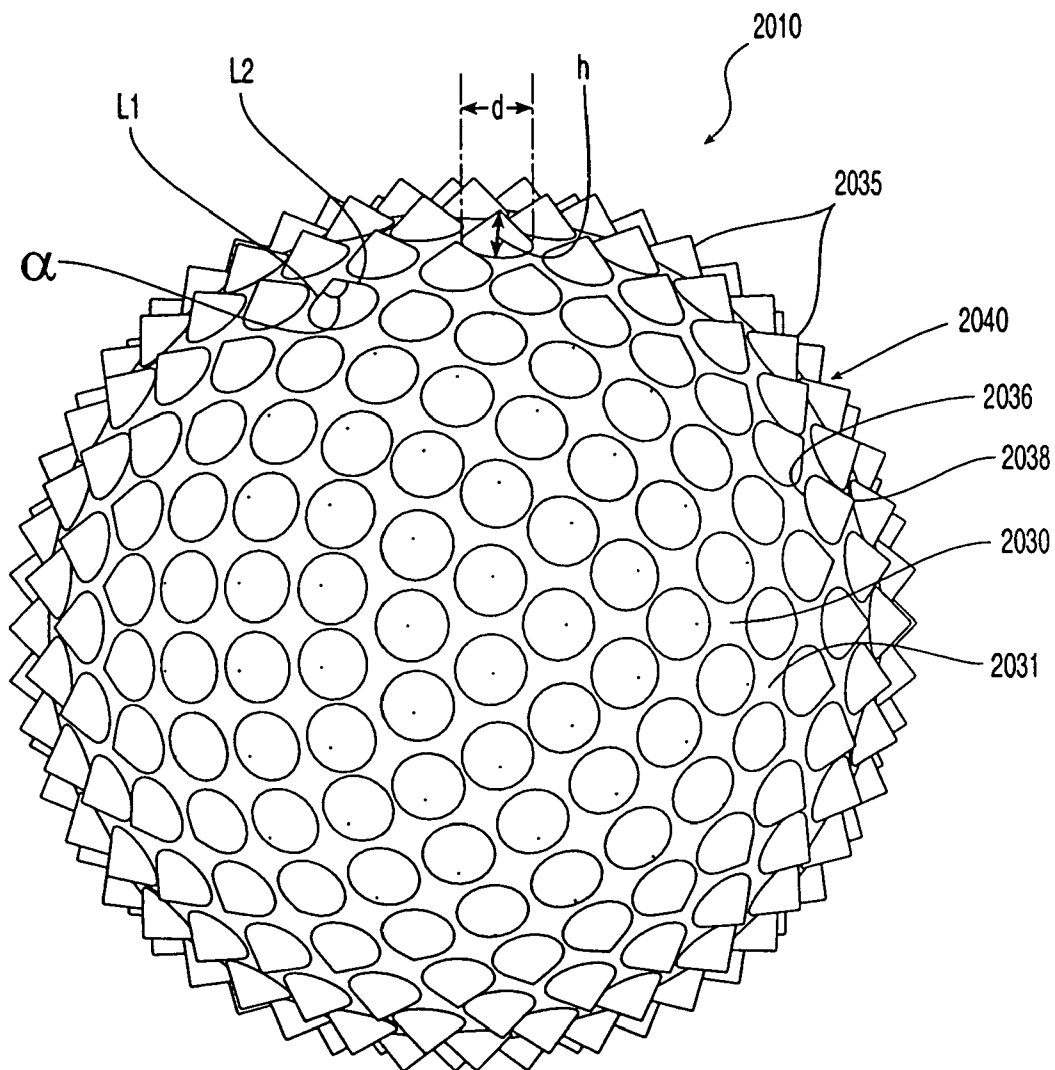


Fig. 13

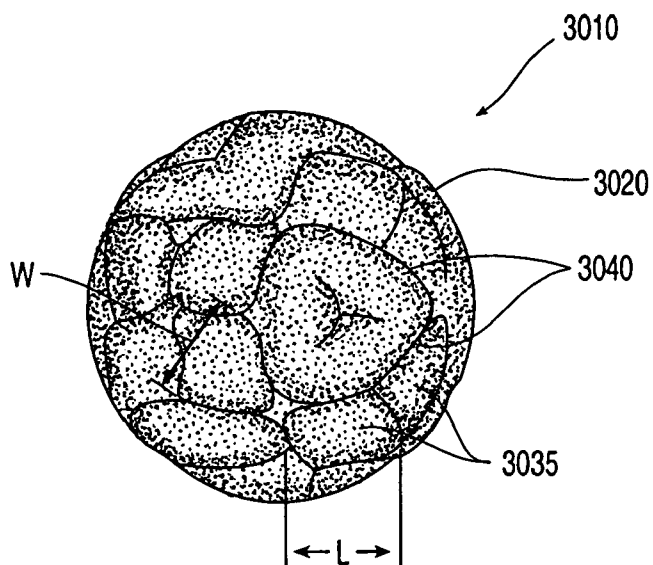


Fig. 14

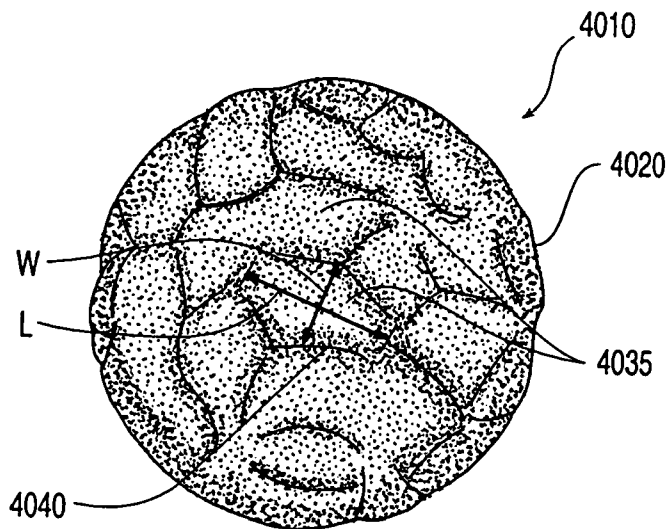


Fig. 15

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GOLF BALLS COMPRISING HIGHLY-NEUTRALIZED ACID POLYMERS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation of U.S. application Ser. No. 10/360,238, which was filed Feb. 6, 2003 now U.S. Pat. No. 6,824,477, which is a continuation-in-part of U.S. application Ser. No. 10/118,719, filed Apr. 9, 2002 now U.S. Pat. No. 6,756,436, which is a non-provisional application claiming priority to U.S. Provisional Application No. 60/301,046, filed Jun. 26, 2001.

FIELD OF THE INVENTION

The present invention is directed to golf ball compositions and, in particular, polymer compositions including highly-neutralized polymers and blends thereof.

BACKGROUND OF THE INVENTION

Conventional golf balls can be divided into two general classes: solid and wound. Solid golf balls include one-piece, two-piece (i.e., solid core and a cover), and multi-layer (i.e., solid core of one or more layers and/or a cover of one or more layers) golf balls. Wound golf balls typically include a solid, hollow, or fluid-filled center, surrounded by a tensioned elastomeric material, and a cover. It is also possible to surround a hollow or fluid-filled center with a plurality of solid layers. Solid balls have traditionally been considered longer and more durable than wound balls, but many solid constructions lack the "feel" provided by the wound construction.

More recently, by altering ball construction and composition, manufacturers have been able to vary a wide range of playing characteristics, such as compression, velocity, "feel," and spin, optimizing each or all be optimized for various playing abilities. In particular, a variety of core and cover layer(s) constructions, such as multi-layer balls having dual cover layers and/or dual core layers, have been investigated and now allow many non-wound balls to exhibit characteristics previously maintainable in a solid-construction golf ball. These golf ball layers are typically constructed with a number of polymeric compositions and blends, including polybutadiene rubber, polyurethanes, polyamides, and ethylene-based ionomers.

Ionomers, and in particular ethylene α,β -ethylenically unsaturated carboxylic acid copolymers or a melt processible ionomer thereof, are a preferred polymer for many golf ball layers. One problem encountered with the use of ionomers as stiff layers, however, is the unprocessability of the material as the percent of neutralization of the acid group increases. Ionomers are stiffened by increasing the amount of neutralization by a metal cation or a salt thereof. Once the percent of neutralization is greater than about 60% (depending on metal cation selected), the melt flow of the ionomer becomes too low and the ease of processability decreases or disappears altogether. For tri-valent cations, the percent neutralization at which the polymer becomes unprocessable can be significantly lower.

There is a need, therefore, for ionomer compositions that are neutralized at high percentages, but in a manner that still allows resultant polymer compositions to be processible. The present invention describes such compositions and there use in a variety of golf ball core and cover layers.

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SUMMARY OF THE INVENTION

The present invention is directed to a golf ball including a core including a polymer containing an acid group neutralized by an organic acid or a salt thereof, the organic acid or salt thereof being present in an amount sufficient to neutralize the polymer by at least about 80%, wherein the core has a first Shore D hardness, a compression of no greater than about 80, and a diameter of no less than about 1.53 inches; and a cover including a material having a second Shore D hardness at least 10 points less than the first hardness.

Additionally, the present invention is also directed to a golf ball including a core including a polymer containing an acid group neutralized by an organic acid or a salt thereof, the organic acid or salt thereof being present in an amount sufficient to neutralize the polymer by at least about 80%, wherein the core has a first Shore D hardness, a compression of no greater than about 80, and a diameter of no less than about 1.53 inches; and a cover including a material having a second Shore D hardness at least 10 points greater than the first hardness.

In one embodiment of the above, the polymer includes ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, thermoplastic elastomers, polybutadiene rubber, balata, grafted metallocene-catalyzed polymers, non-grafted metallocene-catalyzed polymers, single-site polymers, high-crystalline acid polymers, cationic ionomers, and mixtures thereof.

In another embodiment of the above, the organic acid is selected from the group consisting of aliphatic organic acids, aromatic organic acids, saturated mono-functional organic acids, unsaturated mono-functional organic acids, and multi-unsaturated mono-functional organic acids. Preferably, the salt of organic acids include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, calcium, stearic, bebenic, erucic, oleic, linoelic, dimerized derivatives, and mixtures thereof.

In another embodiment of the above, the core further includes a second polymer component in an amount sufficient to reduce the core compression to less than or equal to about 70. Further, preferably the second polymer component has a Shore D hardness of about 40 or greater. It is also preferred that the second polymer component includes ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, thermoplastic elastomers, polybutadiene rubber, balata, grafted metallocene-catalyzed polymers, non-grafted metallocene-catalyzed polymers, single-site polymers, high-crystalline acid polymers, cationic ionomers, and mixtures thereof.

In one embodiment of the above, the organic acid or salt thereof is present in an amount sufficient to neutralize the polymer by at least about 90%. In a preferred embodiment, the organic acid or salt thereof is present in an amount sufficient to neutralize the polymer by at least about 100%. Further, at least one of the polymer or second polymer component is partially neutralized by a metal cation.

In another embodiment, the core has a diameter of about 1.58 inches or greater. The cover may include a castable reactive liquid material or the cover is cast or reaction injection molded over the core. Preferably, the cover includes a polyurethane.

The present invention is also directed to a golf ball including a core including a center and an outer layer, the center including a thermoset rubber and the outer layer

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including polymer neutralized with an organic acid or a salt thereof, the organic acid or salt thereof being present in an amount greater than about 10 weight percent such that the polymer is fully neutralized, wherein the outer layer has a first Shore D hardness and the core has a compression of less than or equal to about 90 and a diameter of about 1.53 inches or greater; and a cover including a castable reactive liquid material having a second Shore D hardness being at least 10 points less than the first hardness.

In one embodiment, the outer layer further includes a softening copolymer in sufficient weight percentage to reduce the core compression to less than or equal to about 70. In another embodiment, the core has a diameter of about 1.58 inches or greater. Preferably, the cover includes a castable reactive liquid material. The cover may also be cast or reaction injection molded over the core. It is preferred that the cover includes a cast polyurethane. In another embodiment, the golf ball further includes an intermediate layer including an ionomer having a Shore D hardness that is at least 10 greater than the first Shore D hardness.

In an alternative embodiment, the core is surface treated by plasma treatment, corona discharge, chemical treatment or mechanically treated.

The present invention is also directed to a golf ball including a core including a thermoset rubber having a diameter of about 0.5 to 1.55 inches; a cover disposed over the core having a shore D hardness of about 55 or less; and an intermediate layer including a polymer neutralized by an organic acid or a salt thereof, the an organic acid or a salt thereof being present in an amount sufficient to neutralize the polymer by at least about 100%.

Preferably, the cover includes a polyurethane. In one embodiment, the intermediate layer has a Shore D hardness of at least about 62. In another embodiment, the cover has a thickness of about 0.04 or less. In still another embodiment, the core has a compression of about 70 or less and a diameter of at least 1.4 inches.

The present invention is also directed to a golf ball including a center including a liquid, the center having a diameter of about 1.0 inches or less; an intermediate layer including a polymer neutralized with an organic acid or a salt thereof, the an organic acid or a salt thereof being present in an amount greater than about 10 weight percent such that the polymer is saturated, the intermediate layer being disposed about the center to form a core; and a cover disposed over the core.

Preferably, the cover includes a polyurethane. Additionally, the core is further including an outer layer including a thermoset rubber disposed between the intermediate layer and the cover. In another embodiment, the outer layer has a hardness that is at least 5 points less than a hardness of the intermediate layer.

The present invention is directed to a golf ball including a core including a polymer containing an acid group fully-neutralized by an organic acid or a salt, a cation source, or a suitable base thereof, the core having a first Shore D hardness, a compression of no greater than about 90, and a diameter of between about 1.00 inches and about 1.64 inches; and a cover layer including ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, thermoplastic elastomers, polybutadiene rubber, balata, grafted metallocene-catalyzed polymers, non-grafted metallocene-catalyzed polymers, single-site polymers, high-crystalline acid polymers and their ionomers, or cationic ionomers. The cation source is selected from a group consisting of metal cations of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, or aluminum.

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The organic acid is selected from the group consisting of aliphatic organic acids, aromatic organic acids, saturated mono-functional organic acids, unsaturated mono-functional organic acids, and multi-unsaturated mono-functional organic acids. The salt of organic acids include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, calcium, stearic, bebenic, erucic, oleic, linoelic, dimerized derivatives, and mixtures thereof. In one embodiment, the cover layer includes a polymer containing an acid group fully-neutralized by an organic acid or a salt, a cation source, or a suitable base thereof. Preferably, the cover layer is formed from a non-castable material.

The polymer includes ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, thermoplastic elastomers, polybutadiene rubber, balata, grafted metallocene-catalyzed polymers, non-grafted metallocene-catalyzed polymers, single-site polymers, high-crystalline acid polymers and their ionomers, cationic ionomers, and mixtures thereof.

The core further includes a second polymer component including ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, thermoplastic elastomers, polybutadiene rubber, balata, grafted metallocene-catalyzed polymers, non-grafted metallocene-catalyzed polymers, single-site polymers, high-crystalline acid polymers, or cationic ionomers, and wherein the second polymer component has a Shore D hardness less than the first hardness and is present in an amount sufficient to reduce the core compression to less than or equal to about 80.

The core can have a diameter of about 1.53 inches or greater or include two or more layers. The cover may be injection molded or compression molded over the core. Ideally, the cover includes an inner cover layer and an outer cover layer. The inner cover may include a polyurethane material, a polyurea material, a polyurethane-urea hybrid material, or a polyurea-urethane hybrid material. At least one of the inner cover or outer cover include a polymer containing an acid group fully-neutralized by an organic acid or a salt, a cation source, or a suitable base thereof.

In one embodiment, the inner cover layer has material hardness of at least about 60 Shore D and the outer cover layer has a material hardness of no greater than about 60 Shore D. In another embodiment, the outer cover layer has material hardness of at least about 60 Shore D and the inner cover layer has a material hardness of no greater than about 60 Shore D. The core compression is no greater than about 80. The core may further include an organosulfur or the metal salt thereof.

The present invention is also directed to a golf ball including a core including a center and an outer core layer, at least one of the center or outer core layer including a polymer containing an acid group fully-neutralized by an organic acid or a salt, a cation source, or a suitable base thereof, the core having a first Shore D hardness, a compression of no greater than about 90, and a diameter of between about 1.00 inches and about 1.64 inches; and a cover layer including ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, thermoplastic elastomers, polybutadiene rubber, balata, grafted metallocene-catalyzed polymers, non-grafted metallocene-catalyzed polymers, single-site polymers, high-crystalline acid polymers and their ionomers, or cationic ionomers fully-neutralized by an organic acid or a salt, a cation source, or a suitable base thereof. The cation source is selected from a

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group consisting of metal cations of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, or aluminum.

The cover layer is an inner cover layer or an outer cover layer. Preferably, the cover layer includes an inner cover layer and an outer cover layer, the outer cover layer including the polymer and the inner cover layer including a polyurethane material, a polyurea material, a polyurethane-urea hybrid material, or a polyurea-urethane hybrid material.

In one embodiment, the inner cover layer has material hardness of at least about 60 Shore D and the outer cover layer has a material hardness of no greater than about 60 Shore D. In another embodiment, the outer cover layer has material hardness of at least about 60 Shore D and the inner cover layer has a material hardness of no greater than about 60 Shore D. The core compression is no greater than about 80.

The present invention is further directed to a golf ball including a core including a solid center and an outer core layer, the core having a first Shore D hardness, a compression of no greater than about 90, and a diameter of between about 1.00 inches and about 1.64 inches; and a first cover layer including a polyurea formed from a polyisocyanate, a polyamine, and a curing agent; wherein at least one of the solid center or the outer core layer includes a polymer containing an acid group fully-neutralized by an organic acid or a salt, a cation source, or a suitable base thereof; and the ball has a compression of between about 50 and about 120. Preferably, the golf ball further includes a second cover layer containing an acid group fully-neutralized by an organic acid or a salt, a cation source, or a suitable base thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is one embodiment of a golf ball of the present invention;

FIG. 2 is a second embodiment of a golf ball of the present invention;

FIG. 3 is a side view of a golf ball according to the present invention;

FIG. 4 is a cross-sectional view along the line 2—2 of FIG. 3 of the golf ball according to the present invention;

FIG. 5 is a side view of an inner core of the golf ball shown in FIG. 4;

FIG. 6 is a plan view along the arrow 4 of FIG. 5 of the inner core according to the present invention;

FIGS. 7–12 are cross-sectional views of other embodiments of golf balls according to the present invention;

FIG. 13 is a perspective view of another embodiment of the inner core according to the present invention;

FIG. 14 is a side view of another embodiment of the inner core according to the present invention; and

FIG. 15 is a side view of another embodiment of the inner core according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to highly-neutralized polymers and blends thereof ("HNP") for the use in golf equipment, preferably in ball cores, intermediate layers, and/or covers. The acid moieties of the HNP's, typically ethylene-based ionomers, are preferably neutralized greater than about 70%, more preferably greater than about 90%, and most preferably at least about 100%. The HNP's can be also be blended with a second polymer component, which,

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if containing an acid group, may be neutralized in a conventional manner, by the organic fatty acids of the present invention, or both. The second polymer component, which may be partially or fully neutralized, preferably comprises ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, polyamides, polycarbonates, polyesters, polyurethanes, polyureas, thermoplastic elastomers, polybutadiene rubber, balata, metallocene-catalyzed polymers (grafted and non-grafted), single-site polymers, high-crystalline acid polymers, cationic ionomers, and the like. HNP polymers typically have a material hardness of between about 20 and about 80 Shore D, and a flexural modulus of between about 3,000 psi and about 200,000 psi.

In one embodiment of the present invention the HNP's are ionomers and/or their acid precursors that are preferably neutralized, either fully or partially, with organic acid copolymers or the salts thereof. The acid copolymers are preferably α -olefin, such as ethylene, C_{3-8} α,β -ethylenically unsaturated carboxylic acid, such as acrylic and methacrylic acid, copolymers. They may optionally contain a softening monomer, such as alkyl acrylate and alkyl methacrylate, wherein the alkyl groups have from 1 to 8 carbon atoms.

The acid copolymers can be described as E/X/Y copolymers where E is ethylene, X is an α,β -ethylenically unsaturated carboxylic acid, and Y is a softening comonomer. In a preferred embodiment, X is acrylic or methacrylic acid and Y is a C_{1-8} alkyl acrylate or methacrylate ester. X is preferably present in an amount from about 1 to about 35 weight percent of the polymer, more preferably from about 5 to about 30 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer. Y is preferably present in an amount from about 0 to about 50 weight percent of the polymer, more preferably from about 5 to about 25 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer.

Specific acid-containing ethylene copolymers include, but are not limited to, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/acrylic acid/ethyl acrylate, ethylene/methacrylic acid/ethyl acrylate, and ethylene/acrylic acid/methyl acrylate copolymers. The most preferred acid-containing ethylene copolymers are, ethylene/(meth)acrylic acid/n-butyl acrylate, ethylene/(meth)acrylic acid/ethyl acrylate, and ethylene/(meth)acrylic acid/methyl acrylate copolymers.

Ionomers are typically neutralized with a metal cation, such as Li, Na, Mg, or Zn. It has been found that by adding sufficient organic acid or salt of organic acid, along with a suitable base, to the acid copolymer or ionomer, however, the ionomer can be neutralized, without losing processability, to a level much greater than for a metal cation. Preferably, the acid moieties are neutralized greater than about 80%, preferably from 90–100%, most preferably 100% without losing processability. This accomplished by melt-blending an ethylene α,β -ethylenically unsaturated carboxylic acid copolymer, for example, with an organic acid or a salt of organic acid, and adding a sufficient amount of a cation source to increase the level of neutralization of all the

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acid moieties (including those in the acid copolymer and in the organic acid) to greater than 90%, (preferably greater than 100%).

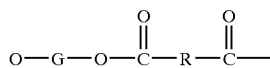
The organic acids of the present invention are aliphatic, mono-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. The salts of organic acids of the present invention include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, salts of fatty acids, particularly stearic, bebenic, erucic, oleic, linoelic or dimerized derivatives thereof. It is preferred that the organic acids and salts of the present invention be relatively non-migratory (they do not bloom to the surface of the polymer under ambient temperatures) and non-volatile (they do not volatilize at temperatures required for melt-blending).

The ionomers of the invention may also be partially neutralized with metal cations. The acid moiety in the acid copolymer is neutralized about 1 to about 100%, preferably at least about 40 to about 100%, and more preferably at least about 90 to about 100%, to form an ionomer by a cation such as lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum, or a mixture thereof.

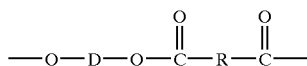
The acid copolymers of the present invention are prepared from 'direct' acid copolymers, copolymers polymerized by adding all monomers simultaneously, or by grafting of at least one acid-containing monomer onto an existing polymer.

Thermoplastic polymer components, such as copolyetheresters, copolyesteresters, copolyetheramides, elastomeric polyolefins, styrene diene block copolymers and their hydrogenated derivatives, copolyesteramides, thermoplastic polyurethanes, such as copolyetherurethanes, copolyesterurethanes, copolyureaurethanes, epoxy-based polyurethanes, polycaprolactone-based polyurethanes, polyureas, and polycarbonate-based polyurethanes fillers, and other ingredients, if included, can be blended in either before, during, or after the acid moieties are neutralized, thermoplastic polyurethanes.

The copolyetheresters are comprised of a multiplicity of recurring long chain units and short chain units joined head-to-tail through ester linkages, the long chain units being represented by the formula:



and the short chain units being represented by the formula:

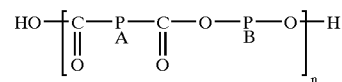


where G is a divalent radical remaining after the removal of terminal hydroxyl groups from a poly (alkylene oxide) glycol having a molecular weight of about 400–8000 and a carbon to oxygen ratio of about 2.0–4.3; R is a divalent radical remaining after removal of hydroxyl groups from a diol having a molecular weight less than about 250; provided said short chain ester units amount to about 15–95 percent by weight of said copolyetherester. The preferred copolyetherester polymers are those where the polyether

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segment is obtained by polymerization of tetrahydrofuran and the polyester segment is obtained by polymerization of tetramethylene glycol and phthalic acid. For purposes of the invention, the molar ether:ester ratio can vary from 90:10 to 10:80; preferably 80:20 to 60:40; and the Shore D hardness is less than 70; preferably less than about 40.

The copolyetheramides are comprised of a linear and regular chain of rigid polyamide segments and flexible polyether segments, as represented by the general formula:



wherein PA is a linear saturated aliphatic polyamide sequence formed from a lactam or amino acid having a hydrocarbon chain containing 4 to 14 carbon atoms or from an aliphatic C₆–C₈ diamine, in the presence of a chain-limiting aliphatic carboxylic diacid having 4–20 carbon atoms; said polyamide having an average molecular weight between 300 and 15,000; and PB is a polyoxyalkylene sequence formed from linear or branched aliphatic polyoxyalkylene glycols, mixtures thereof or copolyethers derived therefrom, said polyoxyalkylene glycols having a molecular weight of less than or equal to 6000; and n indicates a sufficient number of repeating units so that said polyetheramide copolymer has an intrinsic viscosity of from about 0.6 to about 2.05. The preparation of these polyetheramides comprises the step of reacting a dicarboxylic polyamide, the COOH groups of which are located at the chain ends, with a polyoxyalkylene glycol hydroxylated at the chain ends, in the presence of a catalyst such as a tetra-alkyl ortho titanate having the general formula Ti(OR)_x wherein R is a linear branched aliphatic hydrocarbon radical having 1 to 24 carbon atoms. Again, the more polyether units incorporated into the copolyetheramide, the softer the polymer. The ether:amide ratios are as described above for the ether:ester ratios, as is the Shore D hardness.

The elastomeric polyolefins are polymers composed of ethylene and higher primary olefins such as propylene, hexene, octene, and optionally 1,4-hexadiene and or ethylidene norbornene or norbornadiene. The elastomeric polyolefins can be optionally functionalized with maleic anhydride, epoxy, hydroxy, amine, carboxylic acid, sulfonic acid, or thiol groups.

Thermoplastic polyurethanes are linear or slightly chain branched polymers consisting of hard blocks and soft elastomeric blocks. They are produced by reacting soft hydroxy terminated elastomeric polyethers or polyesters with diisocyanates, such as methylene diisocyanate ("MDI"), p-phenylene diisocyanate ("PPDI"), or toluene diisocyanate ("TDI"). These polymers can be chain extended with glycols, secondary diamines, diacids, or amino alcohols. The reaction products of the isocyanates and the alcohols are called urethanes and these blocks are relatively hard and high melting. These hard high melting blocks are responsible for the thermoplastic nature of the polyurethanes.

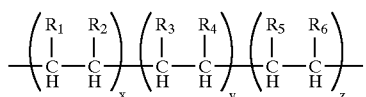
Block styrene diene copolymers and their hydrogenated derivatives are composed of polystyrene units and polydiene units. They may also be functionalized with moieties such as OH, NH₂, epoxy, COOH, and anhydride groups. The polydiene units are derived from polybutadiene, polyisoprene units or copolymers of these two. In the case of the copolymer it is possible to hydrogenate the polyolefin to give a

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saturated rubbery backbone segments. These materials are usually referred to as SBS, SIS, or SEBS thermoplastic elastomers and they can also be functionalized with maleic anhydride.

Grafted metallocene-catalyzed polymers are also useful for blending with the HNP's of the present invention. The grafted metallocene-catalyzed polymers, while conventionally neutralized with metal cations, may also be neutralized, either partially for fully, with organic acids or salts thereof and an appropriate base. Grafted metallocene-catalyzed polymers useful, such as those disclosed in U.S. Pat. Nos. 5,703,166; 5,824,746; 5,981,658; and 6,025,442, which are incorporated herein by reference, in the golf balls of the invention are available in experimental quantities from DuPont under the tradenames SURLYN® NMO 525D, SURLYN® NMO 524D, and SURLYN® NMO 499D, all formerly known as the FUSABOND® family of polymers, or may be obtained by subjecting a non-grafted metallocene-catalyzed polymer to a post-polymerization reaction to provide a grafted metallocene-catalyzed polymer with the desired pendant group or groups. Examples of metallocene-catalyzed polymers to which functional groups may be grafted for use in the invention include, but are not limited to, homopolymers of ethylene and copolymers of ethylene and a second olefin, preferably, propylene, butene, pentene, hexene, heptene, octene, and norbornene. Generally, the invention includes golf balls having at least one layer comprising at least one grafted metallocene-catalyzed polymer or polymer blend, where the grafted metallocene-catalyzed polymer is produced by grafting a functional group onto a metallocene-catalyzed polymer having the formula:



wherein R₁ is hydrogen, branched or straight chain alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl, carbocyclic, or aromatic; R₂ is hydrogen, lower alkyl including C₁-C₅; carbocyclic, or aromatic; R₃ is hydrogen, lower alkyl including C₁-C₅, carbocyclic, or aromatic; R₄ is selected from the group consisting of H, C_nH_{2n+1}, where n=1 to 18, and phenyl, in which from 0 to 5 H within R₄ can be replaced by substituents COOH, SO₃H, NH₂, F, Cl, Br, I, OH, SH, silicone, lower alkyl esters and lower alkyl ethers, with the proviso that R₃ and R₄ can be combined to form a bicyclic ring; R₅ is hydrogen, lower alkyl including C₁-C₅, carbocyclic, or aromatic; R₆ is hydrogen, lower alkyl including C₁-C₅, carbocyclic, or aromatic; and wherein x, y and z are the relative percentages of each co-monomer. X can range from about 1 to 99 percent or more preferably from about 10 to about 70 percent and most preferred, from about 10 to 50 percent. Y can be from 99 to 1 percent, preferably, from 90 to 30 percent, or most preferably, 90 to 50 percent. Z can range from about 0 to about 49 percent. One of ordinary skill in the art would understand that if an acid moiety is present as a ligand in the above polymer that it may be neutralized up to 100% with an organic fatty acid as described above.

Metallocene-catalyzed copolymers or terpolymers can be random or block and may be isotactic, syndiotactic, or atactic. The pendant groups creating the isotactic, syndiotactic, or atactic polymers are chosen to determine the

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interactions between the different polymer chains making up the resin to control the final properties of the resins used in golf ball covers, centers, or intermediate layers. As will be clear to those skilled in the art, grafted metallocene-catalyzed polymers useful in the invention that are formed from metallocene-catalyzed random or block copolymers or terpolymers will also be random or block copolymers or terpolymers, and will have the same tacticity of the metallocene-catalyzed polymer backbone.

As used herein, the term "phrase branched or straight chain alkyl" means any substituted or unsubstituted acyclic carbon-containing compounds. Examples of alkyl groups include lower alkyl, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl or t-butyl; upper alkyl, for example, octyl, nonyl, decyl, and the like; and lower alkylene, for example, ethylene, propylene, butylene, pentene, hexene, octene, norbornene, nonene, decene, and the like.

In addition, such alkyl groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Functional groups include, but are not limited to hydroxyl, amino, carboxyl, sulfonic amide, ester, ether, phosphates, thiol, nitro, silane and halogen (fluorine, chlorine, bromine and iodine), to mention but a few.

As used herein, the term "substituted and unsubstituted carbocyclic" means cyclic carbon-containing compounds, including, but not limited to cyclopentyl, cyclohexyl, cycloheptyl, and the like. Such cyclic groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups having from 1-28 carbon atoms. The cyclic groups of the invention may further comprise a heteroatom.

As mentioned above, R₁ and R₂ can also represent any combination of alkyl, carbocyclic or aryl groups, for example, 1-cyclohexylpropyl, benzyl cyclohexylmethyl, 2-cyclohexylpropyl, 2,2-methylcyclohexylpropyl, 2,2-methylphenylpropyl, and 2,2-methylphenylbutyl.

Non-grafted metallocene-catalyzed polymers useful in the present invention are commercially available under the trade name AFFINITY® polyolefin plastomers and ENGAGE® polyolefin elastomers commercially available from Dow Chemical Company and DuPont-Dow. Other commercially available metallocene-catalyzed polymers can be used, such as EXACT®, commercially available from Exxon and INSIGHT®, commercially available from Dow. The EXACT® and INSIGHT® line of polymers also have novel rheological behavior in addition to their other properties as a result of using a metallocene catalyst technology. Metallocene-catalyzed polymers are also readily available from Sentinel Products Corporation of Hyannis, Mass., as foamed sheets for compression molding.

Monomers useful in the present invention include, but are not limited to, olefinic monomers having, as a functional group, sulfonic acid, sulfonic acid derivatives, such as chlorosulfonic acid, vinyl ethers, vinyl esters, primary, secondary, and tertiary amines, mono-carboxylic acids, dicarboxylic acids, partially or fully ester-derivatized mono-carboxylic and dicarboxylic acids, anhydrides of dicarboxylic acids, and cyclic imides of dicarboxylic acids.

In addition, metallocene-catalyzed polymers may also be functionalized by sulfonation, carboxylation, or the addition of an amine or hydroxy group. Metallocene-catalyzed polymers functionalized by sulfonation, carboxylation, or the addition of a hydroxy group may be converted to anionic ionomers by treatment with a base. Similarly, metallocene-catalyzed polymers functionalized by the addition of an

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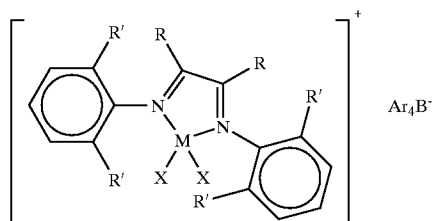
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amine may be converted to cationic ionomers by treatment with an alkyl halide, acid, or acid derivative.

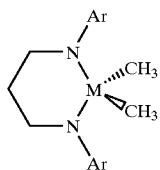
The most preferred monomer is maleic anhydride, which, once attached to the metallocene-catalyzed polymer by the post-polymerization reaction, may be further subjected to a reaction to form a grafted metallocene-catalyzed polymer containing other pendant or functional groups. For example, reaction with water will convert the anhydride to a dicarboxylic acid; reaction with ammonia, alkyl, or aromatic amine forms an amide; reaction with an alcohol results in the formation of an ester; and reaction with base results in the formation of an anionic ionomer.

The HNP's of the present invention may also be blended with single-site and metallocene catalysts and polymers formed therefrom. As used herein, the term "single-site catalyst," such as those disclosed in U.S. Pat. No. 6,150,462 which is incorporated herein by reference, refers to a catalyst that contains an ancillary ligand that influences the steric and electronic characteristics of the polymerizing site in a manner that prevents formation of secondary polymerizing species. The term "metallocene catalyst" refers to a single-site catalyst wherein the ancillary ligands are comprising substituted or unsubstituted cyclopentadienyl groups, and the term "non-metallocene catalyst" refers to a single-site catalyst other than a metallocene catalyst.

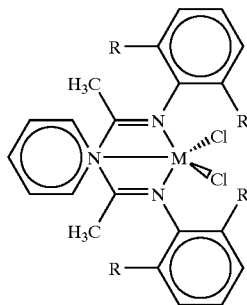
Non-metallocene single-site catalysts include, but are not limited to, the Brookhart catalyst, which has the following structure:



wherein M is nickel or palladium; R and R' are independently hydrogen, hydrocarbyl, or substituted hydrocarbyl; Ar is $(\text{CF}_3)_2\text{C}_6\text{H}_3$, and X is alkyl, methyl, hydride, or halide; the McConville catalyst, which has the structure:

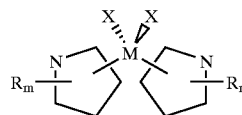


wherein M is titanium or zirconium. Iron (II) and cobalt (II) complexes with 2,6-bis(imino)pyridyl ligands, which have the structure:

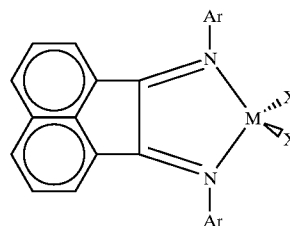


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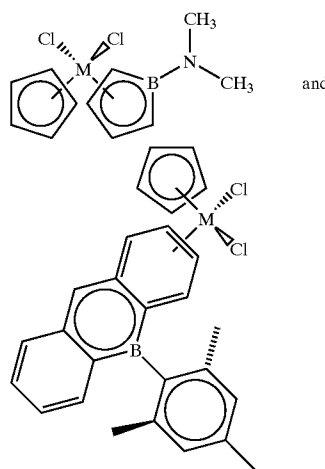
where M is the metal, and R is hydrogen, alkyl, or hydrocarbyl. Titanium or zirconium complexes with pyrroles as ligands also serve as single-site catalysts. These complexes have the structure:



where M is the metal atom; m and n are independently 1 to 4, and indicate the number of substituent groups attached to the aromatic rings; R_m and R_n are independently hydrogen or alkyl; and X is halide or alkyl. Other examples include diimide complexes of nickel and palladium, which have the structure:



where Ar is aromatic, M is the metal, and X is halide or alkyl. Boratabenzene complexes of the Group IV or V metals also function as single-site catalysts. These complexes have the structure:



where B is boron and M is the metal atom.

As used herein, the term "single-site catalyzed polymer" refers to any polymer, copolymer, or terpolymer, and, in particular, any polyolefin polymerized using a single-site catalyst. The term "non-metallocene single-site catalyzed polymer" refers to any polymer, copolymer, or terpolymer, and, in particular, any polyolefin polymerized using a single-site catalyst other than a metallocene-catalyst. The catalysts discussed above are examples of non-metallocene single-site catalysts. The term "metallocene catalyzed polymer"

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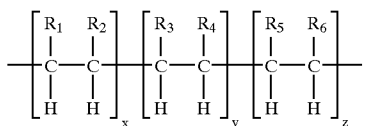
refers to any polymer, copolymer, or terpolymer, and, in particular, any polyolefin, polymerized using a metallocene catalyst.

As used herein, the term "single-site catalyzed polymer blend" refers to any blend of a single-site catalyzed polymer and any other type of polymer, preferably an ionomer, as well as any blend of a single-site catalyzed polymer with another single-site catalyzed polymer, including, but not limited to, a metallocene-catalyzed polymer.

The terms "grafted single-site catalyzed polymer" and "grafted single-site catalyzed polymer blend" refer to any single-site catalyzed polymer or single-site catalyzed polymer blend in which the single-site catalyzed polymer has been subjected to a post-polymerization reaction to graft at least one functional group onto the single-site catalyzed polymer. A "post-polymerization reaction" is any reaction that occurs after the formation of the polymer by a polymerization reaction.

The single-site catalyzed polymer, which may be grafted, may also be blended with polymers, such as non-grafted single-site catalyzed polymers, grafted single-site catalyzed polymers, ionomers, and thermoplastic elastomers. Preferably, the single-site catalyzed polymer is blended with at least one ionomer of the preset invention.

Grafted single-site catalyzed polymers useful in the golf balls of the invention may be obtained by subjecting a non-grafted single-site catalyzed polymer to a post-polymerization reaction to provide a grafted single-site catalyzed polymer with the desired pendant group or groups. Examples of single-site catalyzed polymers to which functional groups may be grafted for use in the invention include, but are not limited to, homopolymers of ethylene and propylene and copolymers of ethylene and a second olefin, preferably, propylene, butene, pentene, hexene, heptene, octene, and norbornene. Monomers useful in the present invention include, but are not limited to olefinic monomers having as a functional group sulfonic acid, sulfonic acid derivatives, such as chlorosulfonic acid, vinyl ethers, vinyl esters, primary, secondary, and tertiary amines, epoxies, isocyanates, mono-carboxylic acids, dicarboxylic acids, partially or fully ester derivatized mono-carboxylic and dicarboxylic acids, anhydrides of dicarboxylic acids, and cyclic imides of dicarboxylic acids. Generally, this embodiment of the invention includes golf balls having at least one layer comprising at least one grafted single-site catalyzed polymer or polymer blend, where the grafted single-site catalyzed polymer is produced by grafting a functional group onto a single-site catalyzed polymer having the formula:



where R_1 is hydrogen, branched or straight chain alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl, carbocyclic, aromatic or heterocyclic; R_2 , R_3 , R_5 , and R_6 are hydrogen, lower alkyl including C_1 - C_5 , carbocyclic, aromatic or heterocyclic; R_4 is H , C_nH_{2n+1} , where $n=1$ to 18, and phenyl, in which from 0 to 5 H within R_4 can be replaced by substituents such as $COOH$, SO_3H , NH_2 , F , Cl , Br , I , OH , SH , epoxy, isocyanate, silicone, lower alkyl esters and lower alkyl ethers; also, R_3 and R_4 can be combined to form a bicyclic ring; and x , y and z are the relative percentages of

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each co-monomer. X can range from about 1 to about 100 percent or more preferably from 1 to 70 percent and most preferred, from about 1 to about 50 percent. Y can be from about 99 to about 0 percent, preferably, from about 9 to about 30 percent, or most preferably, about 9 to about 50 percent. Z can range from about 0 to about 50 percent. One of ordinary skill in the art would also understand that if an acid group is selected as a ligand in the above structure that it too could be neutralized with the organic fatty acids described above.

The HNP's of the present invention may also be blended with high crystalline acid copolymers and their ionomer derivatives (which may be neutralized with conventional metal cations or the organic fatty acids and salts thereof) or a blend of a high crystalline acid copolymer and its ionomer derivatives and at least one additional material, preferably an acid copolymer and its ionomer derivatives. As used herein, the term "high crystalline acid copolymer" is defined as a "product-by-process" in which an acid copolymer or its ionomer derivatives formed from a ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to 200° C., at pressures greater than about 20,000 psi preferably greater than about 25,000 psi, more pref. from about 25,000 psi to about 50,000 psi, wherein up to about 70 percent, preferably 100 percent, of the acid groups are neutralized with a metal ion, organic fatty acids and salts thereof, or a mixture thereof. The copolymer can have a melt index ("MI") of from about 20 to about 300 g/10 min, preferably about 20 to about 200 g/10 min, and upon neutralization of the copolymer, the resulting acid copolymer and its ionomer derivatives should have an MI of from about 0.1 to about 30.0 g/10 min.

Suitable high crystalline acid copolymer and its ionomer derivatives compositions and methods for making them are disclosed in U.S. Pat. No. 5,580,927, the disclosure of which is hereby incorporated by reference in its entirety.

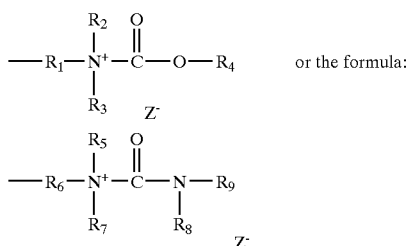
The high crystalline acid copolymer or its ionomer derivatives employed in the present invention are preferably formed from a copolymer containing about 5 to about 35 percent, more preferably from about 9 to about 18, most preferably about 10 to about 13 percent, by weight of acrylic acid, wherein up to about 75 percent, most preferably about 60 percent, of the acid groups are neutralized with an organic fatty acid, salt thereof, or a metal ion, such as sodium, lithium, magnesium, or zinc ion.

Generally speaking, high crystalline acid copolymer and its ionomer derivatives are formed by polymerization of their base copolymers at lower temperatures, but at equivalent pressures to those used for forming a conventional acid copolymer and its ionomer derivatives. Conventional acid copolymers are typically polymerized at a polymerization temperature of from at least about 200° C. to about 270° C., preferably about 220° C., and at pressures of from about 23,000 to about 30,000 psi. In comparison, the high crystalline acid copolymer and its ionomer derivatives employed in the present invention are produced from acid copolymers that are polymerized at a polymerization temperature of less than 200° C., and preferably from about 130° C. to about 200° C., and at pressures from about 20,000 to about 50,000 psi.

The HNP's of the present invention may also be blended with cationic ionomers, such as those disclosed in U.S. Pat. No. 6,193,619 which is incorporated herein by reference. In particular, cationic ionomers have a structure according to the formula:

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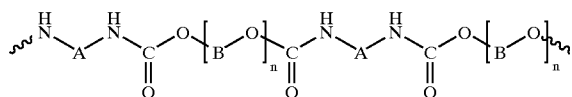


wherein R₁–R₉ are organic moieties of linear or branched chain alkyl, carbocyclic, or aryl; and Z is the negatively charged conjugate ion produced following alkylation and/or quaternization. The cationic polymers may also be quaternized up to 100% by the organic fatty acids described above.

In addition, such alkyl group may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Functional groups include but are not limited to hydroxyl, amino, carboxyl, amide, ester, ether, sulfonic, siloxane, siloxyl, silanes, sulfonyl, and halogen.

As used herein, substituted and unsubstituted carbocyclic groups of up to about 20 carbon atoms means cyclic carbon-containing compounds, including but not limited to cyclopentyl, cyclohexyl, cycloheptyl, and the like. Such cyclic groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups as described above. The cyclic groups of the invention may further comprise a heteroatom.

The HNP's of the present invention may also be blended with polyurethane and polyurea ionomers which include anionic moieties or groups, such as those disclosed in U.S. Pat. No. 6,207,784 which is incorporated herein by reference. Typically, such groups are incorporated onto the diisocyanate or diisocyanate component of the polyurethane or polyurea ionomers. The anionic group can also be attached to the polyol or amine component of the polyurethane or polyurea, respectively. Preferably, the anionic group is based on a sulfonic, carboxylic or phosphoric acid group. Also, more than one type of anionic group can be incorporated into the polyurethane or polyurea. Examples of anionic polyurethane ionomers with anionic groups attached to the diisocyanate moiety can have a chemical structure according to the following formula:



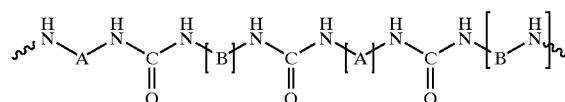
where A=R-Z⁻M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻ or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIA, VIB, VIIB or VIIB metal; x=1 to 5; B is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; and n=1

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to 100. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x} or Hf^{+x}.

Exemplary anionic polyurethane ionomers with anionic groups attached to the polyol component of the polyurethane are characterized by the above chemical structure where A is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; B=R-Z⁻M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻ or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIA, VIB, VIIB or VIIB metal; x=1 to 5; and n=1 to 100. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x} or Hf^{+x}.

Examples of suitable anionic polyurea ionomers with anionic groups attached to the diisocyanate component have a chemical structure according to the following chemical structure:



where A=R-Z⁻M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻ or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIA, VIB, VIIB or VIIB metal; x=1 to 5; and B is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x}, or Hf^{+x}.

Suitable anionic polyurea ionomers with anionic groups attached to the amine component of the polyurea are characterized by the above chemical structure where A is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; B=R-Z⁻M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻ or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIA, VIB, VIIB or VIIB metal; and x=1 to 5. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x}, or Hf^{+x}. The anionic poly polyurea ionomers may also be neutralized up to 100% by the organic fatty acids described above.

The anionic polymers useful in the present invention, such as those disclosed in U.S. Pat. No. 6,221,960 which is incorporated herein by reference, include any homopolymer, copolymer or terpolymer having neutralizable hydroxyl and/or dealkylable ether groups, and in which at least a portion of the neutralizable or dealkylable groups are neutralized or dealkylated with a metal ion.

As used herein "neutralizable" or "dealkylable" groups refer to a hydroxyl or ether group pendent from the polymer chain and capable of being neutralized or dealkylated by a metal ion, preferably a metal ion base. These neutralized polymers have improved properties critical to golf ball performance, such as resiliency, impact strength and toughness and abrasion resistance. Suitable metal bases are ionic compounds comprising a metal cation and a basic anion.

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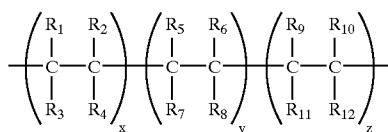
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Examples of such bases include hydroxides, carbonates, acetates, oxides, sulfides, and the like.

The particular base to be used depends upon the nature of the hydroxyl or ether compound to be neutralized or dealkylated, and is readily determined by one skilled in the art. Preferred anionic bases include hydroxides, carbonates, oxides and acetates.

The metal ion can be any metal ion which forms an ionic compound with the anionic base. The metal is not particularly limited, and includes alkali metals, preferably lithium, sodium or potassium; alkaline earth metals, preferably magnesium or calcium; transition metals, preferably titanium, zirconium, or zinc; and Group III and IV metals. The metal ion can have a +1 to +5 charge. Most preferably, the metal is lithium, sodium, potassium, zinc, magnesium, titanium, tungsten, or calcium, and the base is hydroxide, carbonate or acetate.

The anionic polymers useful in the present invention include those which contain neutralizable hydroxyl and/or dealkylable ether groups. Exemplary polymers include ethylene vinyl alcohol copolymers, polyvinyl alcohol, polyvinyl acetate, poly(p-hydroxymethylene styrene), and p-methoxy styrene, to name but a few. It will be apparent to one skilled in the art that many such polymers exist and thus can be used in the compositions of the invention. In general, the anionic polymer can be described by the chemical structure:



where R_1 is OH, $OC(O)R_a$, $O-M^{+V}$, $(CH_2)_nR_b$, $(CHR_z)_nR_b$, or aryl, wherein n is at least 1, R_a is a lower alkyl, M is a metal ion, V is an integer from 1 to 5, R_b is OH, $OC(O)R_a$, $O-M^{+V}$, and R_z is a lower alkyl or aryl, and R_2 , R_3 and R_4 are each independently hydrogen, straight-chain or branched-chain lower alkyl. R_2 , R_3 and R_4 may also be similarly substituted. Preferably n is from 1 to 12, more preferably 1 to 4.

The term "substituted," as used herein, means one or more hydrogen atoms has been replaced by a functional group. Functional groups include, but are not limited to, hydroxyl, amino, carboxyl, sulfonic, amide, ether, ether, phosphates, thiol, nitro, silane, and halogen, as well as many others which are quite familiar to those of ordinary skill in this art.

The terms "alkyl" or "lower alkyl," as used herein, includes a group of from about 1 to 30 carbon atoms, preferably 1 to 10 carbon atoms.

In the anionic polymers useful in the present invention, at least a portion of the neutralizable or dealkylable groups of R_1 are neutralized or dealkylated by an organic fatty acid, a salt thereof, a metal base, or a mixture thereof to form the corresponding anionic moiety. The portion of the neutralizable or dealkylable groups which are neutralized or dealkylated can be between about 1 to about 100 weight percent, preferably between about 50 to about 100 weight percent, more preferably before about 90 to about 100.

Neutralization or dealkylation may be performed by melting the polymer first, then adding a metal ion in an extruder. The degree of neutralization or dealkylation is controlled by varying the amount of metal ion added. Any method of neutralization or dealkylation available to those of ordinary skill in the art may also be suitably employed.

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In one embodiment, the anionic polymer is repeating units any one of the three homopolymer units in the chemical structure above. In a preferred embodiment, R_2 , R_3 and R_4 are hydrogen, and R_1 is hydroxyl, i.e., the anionic polymer is a polyvinyl alcohol homopolymer in which a portion of the hydroxyl groups have been neutralized with a metal base. In another preferred embodiment, R_2 , R_3 and R_4 are hydrogen, R_1 is $OC(O)R_a$, and R_a is methyl, i.e., the anionic polymer is a polyvinyl acetate homopolymer in which a portion of the methyl ether groups have been dealkylated with a metal ion.

The anionic polymer can also be a copolymer of two different repeating units having different substituents, or a terpolymer of three different repeating units described in the above formula. In this embodiment, the polymer can be a random copolymer, an alternating copolymer, or a block copolymer, where the term "copolymer" includes terpolymers.

In another embodiment, the anionic polymer is a copolymer, wherein R_5 , R_6 , R_7 and R_8 are each independently selected from the group defined above for R_2 . The first unit of the copolymer can comprise from about 1 to 99 percent weight percent of the polymer, preferably from about 5 to 50 weight percent, and the second unit of the copolymer can comprise from about 99 to 1 weight percent, preferably from about 95 to 50 weight percent. In one preferred embodiment, the anionic polymer is a random, alternating or block copolymer of units (Ia) and (Ib) wherein R_1 is hydroxyl, and each of the remaining R groups is hydrogen, i.e., the polymer is a copolymer of ethylene and vinyl alcohol. In another preferred embodiment, the anionic polymer is a random, alternating or block copolymer of units (Ia) and (Ib) wherein R_1 is $OC(O)R_5$, where R_5 is methyl, and each of the remaining R groups is hydrogen, i.e., the polymer is a copolymer of ethylene and vinyl acetate.

In another embodiment, the anionic polymer is an anionic polymer having neutralizable hydroxyl and/or dealkylable ether groups of as in the above chemical structure wherein R_{1-9} and R_b and R_z are as defined above; R_{10-11} are each independently selected from the group as defined above for R_2 ; and R_{12} is OH or $OC(O)R_{13}$, where R_{13} is a lower alkyl; wherein x , y and z indicate relative weight percent of the different units. x can be from about 99 to about 50 weight percent of the polymer, y can be from about 1 to about 50 weight percent of the polymer, and z ranges from about 0 to about 50 weight percent of the polymer. At least a portion of the neutralizable groups R_1 are neutralized. When the amount of z is greater than zero, a portion of the groups R_{10} can also be fully or partially neutralized, as desired.

In particular, the anionic polymers and blends thereof can comprise compatible blends of anionic polymers and ionomers, such as the ionomers described above, and ethylene acrylic methacrylic acid ionomers, and their terpolymers, sold commercially under the trade names SURLYN® and IOTEK® by DuPont and Exxon respectively. The anionic polymer blends useful in the golf balls of the invention can also include other polymers, such as polyvinylalcohol, copolymers of ethylene and vinyl alcohol, poly(ethyleneethylene), poly(heptylethylene), poly(hexyldecylethylene), poly(isopentylethylene), poly(butyl acrylate), acrylate, poly(2-ethylbutyl acrylate), poly(heptyl acrylate), poly(2-methylbutyl acrylate), poly(3-methylbutyl acrylate), poly(N-octadecylacrylamide), poly(octadecyl methacrylate), poly(butoxyethylene), poly(methoxyethylene), poly(pentylloxyethylene), poly(1,1-dichloroethylene), poly(4-[(2-butoxyethoxy)methyl]styrene), poly[oxy(ethoxymethyl)ethylene], poly(oxyethylene), poly(oxytetramethylene),

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poly(oxytrimethylene), poly(silanes) and poly(silazanes), polyamides, polycarbonates, polyesters, styrene block copolymers, polyetheramides, polyurethanes, main-chain heterocyclic polymers and poly(furan tetracarboxylic acid diimides), as well as the classes of polymers to which they belong.

The anionic polymer compositions of the present invention typically have a flexural modulus of from about 500 psi to about 300,000 psi, preferably from about 2000 to about 200,000 psi. The anionic polymer compositions typically have a material hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D. The loss tangent, or dissipation factor, is a ratio of the loss modulus over the dynamic shear storage modulus, and is typically less than about 1, preferably less than about 0.01, and more preferably less than about 0.001 for the anionic polymer compositions measured at about 23° C. The specific gravity is typically greater than about 0.7, preferably greater than about 1, for the anionic polymer compositions. The dynamic shear storage modulus, or storage modulus, of the anionic polymer compositions at about 23° C. is typically at least about 10,000 dyn/cm².

The golf balls of the present invention may comprise a variety of constructions. Referring to FIG. 1, in one embodiment of the present invention, golf ball **10** includes a core **12**, an inner cover layer **14** surrounding the core **12**, and an outer cover layer **16**. Preferably, the core **12** is solid.

In a preferred embodiment, the solid core **12** comprises the HNP's of the present invention. In an alternative embodiment, the solid core **12** may include compositions having a base rubber, a crosslinking agent, a filler, and a co-crosslinking or initiator agent, and the inner cover layer **14** comprises the HNP's of the present invention.

The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene having a cis-structure of at least 40%. More preferably, the base rubber comprises high-Mooney-viscosity rubber. If desired, the polybutadiene can also be mixed with other elastomers known in the art such as natural rubber, polyisoprene rubber and/or styrene-butadiene rubber in order to modify the properties of the core.

The crosslinking agent includes a metal salt of an unsaturated fatty acid such as a zinc salt or a magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms such as acrylic or methacrylic acid. Suitable cross linking agents include metal salt diacrylates, dimethacrylates and monomethacrylates wherein the metal is magnesium, calcium, zinc, aluminum, sodium, lithium or nickel. The crosslinking agent is present in an amount from about 15 to about 30 parts per hundred of the rubber, preferably in an amount from about 19 to about 25 parts per hundred of the rubber and most preferably having about 20 to 24 parts crosslinking agent per hundred of rubber. The core compositions of the present invention may also include at least one organic or inorganic cis-trans catalyst to convert a portion of the cis-isomer of polybutadiene to the trans-isomer, as desired.

The initiator agent can be any known polymerization initiator which decomposes during the cure cycle. Suitable initiators include peroxide compounds such as dicumyl peroxide, 1,1-di-(t-butylperoxy) 3,3,5-trimethyl cyclohexane, a-a bis-(t-butylperoxy)diisopropylbenzene, 2,5-dimethyl-2,5 di-(t-butylperoxy)hexane or di-t-butyl peroxide and mixtures thereof.

Fillers, any compound or composition that can be used to vary the density and other properties of the core, typically

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include materials such as tungsten, zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate, metals, metal oxides and salts, regrind (recycled core material typically ground to about 30 mesh particle), high-Mooney-viscosity rubber regrind, and the like.

The golf ball cores of the present invention may also comprise a variety of constructions. For example, the core may comprise a single layer or a plurality of layers. The core may also comprise a formed of a tensioned elastomeric material. Referring to FIG. 2, in another embodiment of the present invention, golf ball **20** comprises a solid center **22** surrounded by at least one additional solid outer core layer **24**. The "dual" core **26** is surrounded by a "double" cover **28** comprising an inner cover layer **30** and an outer cover layer **32**.

Preferably, the solid center **22** comprises the HNP's of the present invention. In another embodiment, the inner cover layer **28** comprises the highly-neutralized acid copolymers of the present invention. In an alternative embodiment, the outer core layer **24** comprises the highly-neutralized acid copolymers of the present invention.

At least one of the outer core layers is formed of a resilient rubber-based component comprising a high-Mooney-viscosity rubber, and a crosslinking agent present in an amount from about 20 to about 40 parts per hundred, from about 30 to about 38 parts per hundred, and most preferably about 37 parts per hundred. It should be understood that the term "parts per hundred" is with reference to the rubber by weight.

When the golf ball of the present invention includes an intermediate layer, such as an outer core layer or an inner cover layer, any or all of these layer(s) may comprise thermoplastic and thermosetting material, but preferably the intermediate layer(s), if present, comprise any suitable material, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid which are available under the trademark SURLYN® of E.I. DuPont de Nemours & Co., of Wilmington, Del., or IOTEK® or ESCOR® of Exxon. These are copolymers or terpolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel or the like, in which the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include methacrylic, crotonic, maleic, fumaric or itaconic acid.

This golf ball can likewise include one or more homopolymeric or copolymeric inner cover materials, such as:

- (1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;
- (2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst;
- (3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates, in particular PPDI-based thermoplastic polyurethanes, and those disclosed in U.S. Pat. No. 5,334,673;
- (4) Polyureas, such as those disclosed in U.S. Pat. No. 5,484,870;

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- (5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly(caprolactam), and blends of polyamides with SURLYN®, polyethylene, ethylene copolymers, ethylene-propylene-non-conjugated diene terpolymer, and the like;
- (6) Acrylic resins and blends of these resins with polyvinyl chloride, elastomers, and the like;
- (7) Thermoplastics, such as urethane; olefinic thermoplastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer; block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly(ether-amide), such as PEBAX®, sold by ELF Atochem of Philadelphia, Pa.;
- (8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene as sold under the trademark NORYL® by General Electric Company of Pittsfield, Mass.;
- (9) Thermoplastic polyesters, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified, poly(trimethylene terephthalate), and elastomers sold under the trademarks HYTREL® by E.I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD® by General Electric Company of Pittsfield, Mass.;
- (10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene or ethylene vinyl acetate or other elastomers; and
- (11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

Preferably, the inner cover includes polymers, such as ethylene, propylene, butene-1 or hexane-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. More preferably, in a low spin rate embodiment designed for maximum distance, the acrylic or methacrylic acid is present in about 16 to 35 weight percent, making the ionomer a high modulus ionomer. In a higher spin embodiment, the inner cover layer includes an ionomer where an acid is present in about 10 to 15 weight percent and includes a softening comonomer. Additionally, high-density polyethylene ("HDPE"), low-density polyethylene ("LDPE"), LLDPE, and homo- and co-polymers of polyolefin are suitable for a variety of golf ball layers.

In one embodiment, the outer cover preferably includes a polyurethane composition comprising the reaction product of at least one polyisocyanate, polyol, and at least one curing

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agent. Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"); polymeric MDI; carbodiimide-modified liquid MDI; 4,4'-dicyclohexylmethane diisocyanate ("H₁₂MDI"); p-phenylene diisocyanate ("PPDI"); m-phenylene diisocyanate ("MPDI"); toluene diisocyanate ("TDI"); 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"); isophoronediiisocyanate ("IPDI"); hexamethylene diisocyanate ("HDI"); naphthalene diisocyanate ("NDI"); xylene diisocyanate ("XDI"); p-tetramethylxylene diisocyanate ("p-TMXDI"); m-tetramethylxylene diisocyanate ("m-TMXDI"); ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate ("TMDI"); tetracene diisocyanate; naphthalene diisocyanate; anthracene diisocyanate; isocyanurate of toluene diisocyanate; uretdione of hexamethylene diisocyanate; and mixtures thereof. Polyisocyanates are known to those of ordinary skill in the art as having more than one isocyanate group, e.g., di-isocyanate, tri-isocyanate, and tetra-isocyanate. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term "MDI" includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 7.5% NCO, and more preferably, less than about 7.0%.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol. Examples include, but are not limited to, polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

In another embodiment, polyester polyols are included in the polyurethane material of the invention. Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol; polybutylene adipate glycol; polyethylene propylene adipate glycol; o-phthalate-1,6-hexanediol; poly(hexamethylene adipate)glycol; and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In another embodiment, polycaprolactone polyols are included in the materials of the invention. Suitable polycaprolactone polyols are included in the materials of the invention. Suitable polycaprolactone polyols are included in the materials of the invention.

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prolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In yet another embodiment, the polycarbonate polyols are included in the polyurethane material of the invention. Suitable polycarbonates include, but are not limited to, polyphthalate carbonate and poly(hexamethylene carbonate) glycol. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups. In one embodiment, the molecular weight of the polyol is from about 200 to about 4000.

Polyamine curatives are also suitable for use in the polyurethane composition of the invention and have been found to improve cut, shear, and impact resistance of the resultant balls. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,6-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline) ("MCDEA"); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkylidiamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine ("MPDA"); 4,4'-methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-methylene-bis-(2,6-diethylaniline) ("MDEA"); 4,4'-methylene-bis-(2,3-dichloroaniline) ("MDCA"); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2', 3,3'-tetrachloro diamino diphenylmethane; trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as ETHACURE 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives, which include both primary and secondary amines, preferably have molecular weights ranging from about 64 to about 2000.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β-hydroxyethyl)ether; hydroquinone-di-(β-hydroxyethyl)ether; and mixtures thereof. Preferred hydroxy-terminated curatives include 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol, and mixtures thereof. Preferably, the hydroxy-terminated curatives have molecular weights ranging from about 48 to 2000. It should be understood that molecular weight, as used herein, is the absolute weight average molecular weight and would be understood as such by one of ordinary skill in the art.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups.

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The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

In a preferred embodiment of the present invention, saturated polyurethanes used to form cover layers, preferably the outer cover layer, and may be selected from among both castable thermoset and thermoplastic polyurethanes.

In this embodiment, the saturated polyurethanes of the present invention are substantially free of aromatic groups or moieties. Saturated polyurethanes suitable for use in the invention are a product of a reaction between at least one polyurethane prepolymer and at least one saturated curing agent. The polyurethane prepolymer is a product formed by a reaction between at least one saturated polyol and at least one saturated diisocyanate. As is well known in the art, a catalyst may be employed to promote the reaction between the curing agent and the isocyanate and polyol.

Saturated diisocyanates which can be used include, without limitation, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; dicyclohexylmethane diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isophorone diisocyanate ("IPDI"); methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate ("TMDI"). The most preferred saturated diisocyanates are 4,4'-dicyclohexylmethane diisocyanate ("HMDI") and isophorone diisocyanate ("IPDI").

Saturated polyols which are appropriate for use in this invention include without limitation polyether polyols such as polytetramethylene ether glycol and poly(oxypropylene) glycol. Suitable saturated polyester polyols include polyethylene adipate glycol, polyethylene propylene adipate glycol, polybutylene adipate glycol, polycarbonate polyol and ethylene oxide-capped polyoxypropylene diols. Saturated polycaprolactone polyols which are useful in the invention include diethylene glycol-initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, 1,6-hexanediol-initiated polycaprolactone; trimethylol propane-initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, and polytetramethylene ether glycol-initiated polycaprolactone. The most preferred saturated polyols are polytetramethylene ether glycol and PTMEG-initiated polycaprolactone.

Suitable saturated curatives include 1,4-butanediol, ethylene glycol, diethylene glycol, polytetramethylene ether glycol, propylene glycol; trimethanolpropane; tetra-(2-hydroxypropyl)-ethylenediamine; isomers and mixtures of isomers of cyclohexyldimethylol, isomers and mixtures of isomers of cyclohexane bis(methylamine); triisopropanolamine; ethylene diamine; diethylene triamine; triethylene tetramine; tetraethylene pentamine; 4,4'-dicyclohexylmethane diamine; 2,2,4-trimethyl-1,6-hexanediamine; 2,4,4-trimethyl-1,6-hexanediamine; diethyleneglycol di-(aminopropyl)ether; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,2-bis-(sec-butylamino)cyclohexane; 1,4-bis-(sec-butylamino)cyclohexane; isophorone diamine; hexamethylene diamine; propylene diamine; 1-methyl-2,4-cyclohexyl diamine; 1-methyl-2,6-cyclohexyl diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; imido-bis-propylamine; isomers and mixtures of isomers of diaminocyclo-

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hexane; monoethanolamine; diethanolamine; triethanolamine; monoisopropanolamine; and diisopropanolamine. The most preferred saturated curatives are 1,4-butanediol, 1,4-cyclohexyldimethylol and 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

The compositions of the invention may also be polyurea-based, which are distinctly different from polyurethane compositions, but also result in desirable aerodynamic and aesthetic characteristics when used in golf ball components. The polyurea-based compositions are preferably saturated in nature.

Without being bound to any particular theory, it is now believed that substitution of the long chain polyol segment in the polyurethane prepolymer with a long chain polyamine oligomer soft segment to form a polyurea prepolymer, improves shear, cut, and resiliency, as well as adhesion to other components. Thus, the polyurea compositions of this invention may be formed from the reaction product of an isocyanate and polyamine prepolymer crosslinked with a curing agent. For example, polyurea-based compositions of the invention may be prepared from at least one isocyanate, at least one polyether amine, and at least one diol curing agent or at least one diamine curing agent.

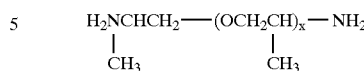
Any polyamine available to one of ordinary skill in the art is suitable for use in the polyurea prepolymer. Polyether amines are particularly suitable for use in the prepolymer. As used herein, "polyether amines" refer to at least polyoxyalkyleneamines containing primary amino groups attached to the terminus of a polyether backbone. Due to the rapid reaction of isocyanate and amine, and the insolubility of many urea products, however, the selection of diamines and polyether amines is limited to those allowing the successful formation of the polyurea prepolymers. In one embodiment, the polyether backbone is based on tetramethylene, propylene, ethylene, trimethylolpropane, glycerin, and mixtures thereof.

Suitable polyether amines include, but are not limited to, methyldiethanolamine; polyoxyalkylenediamines such as, polytetramethylene ether diamines, polyoxypropylenetriamine, and polyoxypropylene diamines; poly(ethylene oxide capped oxypropylene)ether diamines; propylene oxide-based triamines; triethyleneglycoldiamines; trimethylolpropane-based triamines; glycerin-based triamines; and mixtures thereof. In one embodiment, the polyether amine used to form the prepolymer is JEFFAMINE® D2000 (manufactured by Huntsman Chemical Co. of Austin, Tex.).

The molecular weight of the polyether amine for use in the polyurea prepolymer may range from about 100 to about 5000. As used herein, the term "about" is used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range. In one embodiment, the polyether amine molecular weight is about 200 or greater, preferably about 230 or greater. In another embodiment, the molecular weight of the polyether amine is about 4000 or less. In yet another embodiment, the molecular weight of the polyether amine is about 600 or greater. In still another embodiment, the molecular weight of the polyether amine is about 3000 or less. In yet another embodiment, the molecular weight of the polyether amine is between about 1000 and about 3000, and more preferably is between about 1500 to about 2500. Because lower molecular weight polyether amines may be prone to forming solid polyureas, a higher molecular weight oligomer, such as Jeffamine D2000, is preferred.

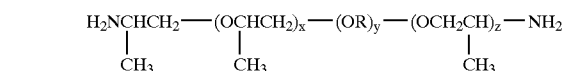
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In one embodiment, the polyether amine has the generic structure:



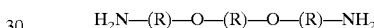
wherein the repeating unit x has a value ranging from about 1 to about 70. Even more preferably, the repeating unit may be from about 5 to about 50, and even more preferably is from about 12 to about 35.

In another embodiment, the polyether amine has the generic structure:



wherein the repeating units x and z have combined values from about 3.6 to about 8 and the repeating unit y has a value ranging from about 9 to about 50, and wherein R is $\text{---}(\text{CH}_2)_a\text{---}$, where "a" may be a repeating unit ranging from about 1 to about 10.

In yet another embodiment, the polyether amine has the generic structure:



wherein R is $\text{---}(\text{CH}_2)_a\text{---}$, and "a" may be a repeating unit ranging from about 1 to about 10.

As briefly discussed above, some amines may be unsuitable for reaction with the isocyanate because of the rapid reaction between the two components. In particular, shorter chain amines are fast reacting. In one embodiment, however, a hindered secondary diamine may be suitable for use in the prepolymer. Without being bound to any particular theory, it is believed that an amine with a high level of steric hindrance, e.g., a tertiary butyl group on the nitrogen atom, has a slower reaction rate than an amine with no hindrance or a low level of hindrance. For example, 4,4'-bis-(sec-butylamino)-dicyclohexylmethane (CLEARLINK® 1000) may be suitable for use in combination with an isocyanate to form the polyurea prepolymer.

Any isocyanate available to one of ordinary skill in the art is suitable for use in the polyurea prepolymer. Isocyanates for use with the present invention include aliphatic, cycloaliphatic, araliphatic, aromatic, any derivatives thereof, and combinations of these compounds having two or more isocyanate (NCO) groups per molecule. The isocyanates may be organic polyisocyanate-terminated prepolymers. The isocyanate-containing reactable component may also include any isocyanate-functional monomer, dimer, trimer, or multimeric adduct thereof, prepolymer, quasi-prepolymer, or mixtures thereof. Isocyanate-functional compounds may include monoisocyanates or polyisocyanates that include any isocyanate functionality of two or more.

Suitable isocyanate-containing components include diisocyanates having the generic structure: $\text{O}=\text{C}=\text{N---R---N}=\text{C}=\text{O}$, where R is preferably a cyclic, aromatic, or linear or branched hydrocarbon moiety containing from about 1 to about 20 carbon atoms. The diisocyanate may also contain one or more cyclic groups or one or more phenyl groups. When multiple cyclic or aromatic groups are present, linear and/or branched hydrocarbons

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containing from about 1 to about 10 carbon atoms can be present as spacers between the cyclic or aromatic groups. In some cases, the cyclic or aromatic group(s) may be substituted at the 2-, 3-, and/or 4-positions, or at the ortho-, meta-, and/or para-positions, respectively. Substituted groups may include, but are not limited to, halogens, primary, secondary, or tertiary hydrocarbon groups, or a mixture thereof.

Examples of diisocyanates that can be used with the present invention include, but are not limited to, substituted and isomeric mixtures including 2,2', 2,4', and 4,4'-diphenylmethane diisocyanate (MDI); 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI); toluene diisocyanate (TDI); polymeric MDI; carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate; para-phenylene diisocyanate (PPDI); meta-phenylene diisocyanate (MPDI); triphenyl methane-4,4'- and triphenyl methane-4,4'-triisocyanate; naphthylene-1,5-diisocyanate; 2,4', 4,4', and 2,2-biphenyl diisocyanate; polyphenyl polymethylene polyisocyanate (PMDI); mixtures of MDI and PMDI; mixtures of PMDI and TDI; ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,2-diisocyanate; tetramethylene-1,3-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate (HDI); octamethylene diisocyanate; decamethylene diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,1 2-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl-cyclohexylene diisocyanate (HTDI); 2,4-methylcyclohexane diisocyanate; 2,6-methylcyclohexane diisocyanate; 4,4'-dicyclohexyl diisocyanate; 2,4'-dicyclohexyl diisocyanate; 1,3,5-cyclohexane triisocyanate; isocyanatomethylcyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isocyanatoethylcyclohexane isocyanate; bis (isocyanatomethyl)-cyclohexane diisocyanate; 4,4'-bis (isocyanatomethyl)dicyclohexane; 2,4'-bis (isocyanatomethyl)dicyclohexane; isophorone diisocyanate (IPDI); triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate (TMDI); 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI); 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; 1,2-, 1,3-, and 1,4-phenylene diisocyanate; aromatic aliphatic isocyanate, such as 1,2-, 1,3-, and 1,4-xylene diisocyanate; meta-tetramethylxylene diisocyanate (m-TMXDI); para-tetramethylxylene diisocyanate (p-TMXDI); trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylxylene diisocyanate, isocyanurate of hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate, and mixtures thereof; dimerized uretdione of any polyisocyanate, such as uretdione of toluene diisocyanate, uretdione of hexamethylene diisocyanate, and mixtures thereof; modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof.

Examples of saturated diisocyanates that can be used with the present invention include, but are not limited to, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate (HDI); octamethylene diisocyanate; decamethylene diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl-cyclohexylene diisocyanate (HTDI); 2,4-methylcyclohexane diisocyanate; 2,6-methylcyclohexane diisocyanate; 4,4'-dicyclohexyl diisocyanate; 2,4'-dicyclohexyl diisocyanate; 1,3,5-cyclo-

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hexane triisocyanate; isocyanatomethylcyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isocyanatoethylcyclohexane isocyanate; bis (isocyanatomethyl)-cyclohexane diisocyanate; 4,4'-bis (isocyanatomethyl)dicyclohexane; 2,4'-bis (isocyanatomethyl)dicyclohexane; isophorone diisocyanate (IPDI); triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate (TMDI); 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI); 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; and mixtures thereof. Aromatic aliphatic isocyanates may also be used to form light stable materials. Examples of such isocyanates include 1,2-, 1,3-, and 1,4-xylene diisocyanate; meta-tetramethylxylene diisocyanate (m-TMXDI); para-tetramethylxylene diisocyanate (p-TMXDI); trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylxylene diisocyanate, isocyanurate of hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate, and mixtures thereof, dimerized uretdione of any polyisocyanate, such as uretdione of toluene diisocyanate, uretdione of hexamethylene diisocyanate, and mixtures thereof, modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof. In addition, the aromatic aliphatic isocyanates may be mixed with any of the saturated isocyanates listed above for the purposes of this invention.

The number of unreacted NCO groups in the polyurea prepolymer of isocyanate and polyether amine may be varied to control such factors as the speed of the reaction, the resultant hardness of the composition, and the like. For instance, the number of unreacted NCO groups in the polyurea prepolymer of isocyanate and polyether amine may be less than about 14 percent. In one embodiment, the polyurea prepolymer has from about 5 percent to about 11 percent unreacted NCO groups, and even more preferably has from about 6 to about 9.5 percent unreacted NCO groups. In one embodiment, the percentage of unreacted NCO groups is about 3 percent to about 9 percent. Alternatively, the percentage of unreacted NCO groups in the polyurea prepolymer may be about 7.5 percent or less, and more preferably, about 7 percent or less. In another embodiment, the unreacted NCO content is from about 2.5 percent to about 7.5 percent, and more preferably from about 4 percent to about 6.5 percent.

When formed, polyurea prepolymers may contain about 10 percent to about 20 percent by weight of the prepolymer of free isocyanate monomer. Thus, in one embodiment, the polyurea prepolymer may be stripped of the free isocyanate monomer. For example, after stripping, the prepolymer may contain about 1 percent or less free isocyanate monomer. In another embodiment, the prepolymer contains about 0.5 percent by weight or less of free isocyanate monomer.

The polyether amine may be blended with additional polyols to formulate copolymers that are reacted with excess isocyanate to form the polyurea prepolymer. In one embodiment, less than about 30 percent polyol by weight of the copolymer is blended with the saturated polyether amine. In another embodiment, less than about 20 percent polyol by weight of the copolymer, preferably less than about 15 percent by weight of the copolymer, is blended with the polyether amine. The polyols listed above with respect to the polyurethane prepolymer, e.g., polyether polyols, polycaprolactone polyols, polyester polyols, polycarbonate polyols, hydrocarbon polyols, other polyols, and mixtures thereof, are also suitable for blending with the polyether amine. The molecular weight of these polymers may be from

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about 200 to about 4000, but also may be from about 1000 to about 3000, and more preferably are from about 1500 to about 2500.

The polyurea composition can be formed by crosslinking the polyurea prepolymer with a single curing agent or a blend of curing agents. The curing agent of the invention is preferably an amine-terminated curing agent, more preferably a secondary diamine curing agent so that the composition contains only urea linkages. In one embodiment, the amine-terminated curing agent may have a molecular weight of about 64 or greater. In another embodiment, the molecular weight of the amine-curing agent is about 2000 or less. As discussed above, certain amine-terminated curing agents may be modified with a compatible amine-terminated freezing point depressing agent or mixture of compatible freezing point depressing agents.

Suitable amine-terminated curing agents include, but are not limited to, ethylene diamine; hexamethylene diamine; 1-methyl-2,6-cyclohexyl diamine; tetrahydroxypropylene ethylene diamine; 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 4,4'-dicyclohexylmethane diamine; 1,4-cyclohexane-bis-(methylamine); 1,3-cyclohexane-bis-(methylamine); diethylene glycol di-(aminopropyl)ether; 2-methylpentamethylene-diamine; diaminocyclohexane; diethylene triamine; triethylene tetramine; tetraethylene pentamine; propylene diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; dipropylene triamine; imido-bis-propylamine; monoethanolamine, diethanolamine; triethanolamine; monoisopropanolamine, diisopropanolamine; isophoronediamine; 4,4'-methylenebis-(2-chloroaniline); 3,5-dimethylthio-2,4-toluenediamine; 3,5-dimethylthio-2,6-toluenediamine; 3,5-diethylthio-2,4-toluenediamine; 3,5-diethylthio-2,6-toluenediamine; 4,4'-bis-(sec-butylamino)-diphenylmethane and derivatives thereof; 1,4-bis-(sec-butylamino)-benzene; 1,2-bis-(sec-butylamino)-benzene; N,N'-dialkylamino-diphenylmethane; N,N,N',N'-tetrakis (2-hydroxypropyl)ethylene diamine; trimethyleneglycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; 4,4'-methylenebis-(3-chloro-2,6-diethylenylaniline); 4,4'-methylenebis-(2,6-diethylaniline); meta-phenylenediamine; paraphenylenediamine; and mixtures thereof. In one embodiment, the amine-terminated curing agent is 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

Suitable saturated amine-terminated curing agents include, but are not limited to, ethylene diamine; hexamethylene diamine; 1-methyl-2,6-cyclohexyl diamine; tetrahydroxypropylene ethylene diamine; 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 4,4'-dicyclohexylmethane diamine; 4,4'-methylenebis-(2,6-diethylaminocyclohexane; 1,4-cyclohexane-bis-(methylamine); 1,3-cyclohexane-bis-(methylamine); diethylene glycol di-(aminopropyl)ether; 2-methylpentamethylene-diamine; diaminocyclohexane; diethylene triamine; triethylene tetramine; tetraethylene pentamine; propylene diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; imido-bis-propylamine; monoethanolamine, diethanolamine; triethanolamine; monoisopropanolamine, diisopropanolamine; isophoronediamine; triisopropanolamine; and mixtures thereof.

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In addition, any of the polyether amines listed above may be used as curing agents to react with the polyurea prepolymers.

Suitable catalysts include, but are not limited to bismuth catalyst, oleic acid, triethylenediamine (DABCO®-33LV), di-butyltin dilaurate (DABCO®-T12) and acetic acid. The most preferred catalyst is di-butyltin dilaurate (DABCO®-T12). DABCO® materials are manufactured by Air Products and Chemicals, Inc.

Thermoplastic materials may be blended with other thermoplastic materials, but thermosetting materials are difficult if not impossible to blend homogeneously after the thermosetting materials are formed. Preferably, the saturated polyurethane comprises from about 1% to about 100%, more preferably from about 10% to about 75% of the cover composition and/or the intermediate layer composition. About 90% to about 10%, more preferably from about 90% to about 25% of the cover and/or the intermediate layer composition is comprised of one or more other polymers and/or other materials as described below. Such polymers include, but are not limited to polyurethane/polyurea ionomers, polyurethanes or polyureas, epoxy resins, polyethylenes, polyamides and polyesters, polycarbonates and polyacrylin. Unless otherwise stated herein, all percentages are given in percent by weight of the total composition of the golf ball layer in question.

Polyurethane prepolymers are produced by combining at least one polyol, such as a polyether, polycaprolactone, polycarbonate or a polyester, and at least one isocyanate. Thermosetting polyurethanes are obtained by curing at least one polyurethane prepolymer with a curing agent selected from a polyamine, triol or tetraol. Thermoplastic polyurethanes are obtained by curing at least one polyurethane prepolymer with a diol curing agent. The choice of the curatives is critical because some urethane elastomers that are cured with a diol and/or blends of diols do not produce urethane elastomers with the impact resistance required in a golf ball cover. Blending the polyamine curatives with diol cured urethane elastomeric formulations leads to the production of thermoset urethanes with improved impact and cut resistance.

Thermoplastic polyurethanes may be blended with suitable materials to produce a thermoplastic end product. Examples of such additional materials may include ionomers such as the SURLYN®, ESCOR® and IOTEK® copolymers described above.

Other suitable materials which may be combined with the saturated polyurethanes in forming the cover and/or intermediate layer(s) of the golf balls of the invention include ionic or non-ionic polyurethanes and polyureas, epoxy resins, polyethylenes, polyamides and polyesters. For example, the cover and/or intermediate layer may be formed from a blend of at least one saturated polyurethane and thermoplastic or thermoset ionic and non-ionic urethanes and polyurethanes, cationic urethane ionomers and urethane epoxies, ionic and non-ionic polyureas and blends thereof. Examples of suitable urethane ionomers are disclosed in U.S. Pat. No. 5,692,974 entitled "Golf Ball Covers", the disclosure of which is hereby incorporated by reference in its entirety. Other examples of suitable polyurethanes are described in U.S. Pat. No. 5,334,673. Examples of appropriate polyureas are discussed in U.S. Pat. No. 5,484,870 and examples of suitable polyurethanes cured with epoxy group containing curing agents are disclosed in U.S. Pat. No. 5,908,358, the disclosures of which are hereby incorporated herein by reference in their entirety.

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A variety of conventional components can be added to the cover compositions of the present invention. These include, but are not limited to, white pigment such as TiO_2 , ZnO , optical brighteners, surfactants, processing aids, foaming agents, density-controlling fillers, UV stabilizers and light stabilizers. Saturated polyurethanes are resistant to discoloration. However, they are not immune to deterioration in their mechanical properties upon weathering. Addition of UV absorbers and light stabilizers therefore helps to maintain the tensile strength and elongation of the saturated polyurethane elastomers. Suitable UV absorbers and light stabilizers include TINUVIN® 328, TINUVIN® 213, TINUVIN® 765, TINUVIN® 770 and TINUVIN® 622. The preferred UV absorber is TINUVIN® 328, and the preferred light stabilizer is TINUVIN® 765. TINUVIN® products are available from Ciba-Geigy. Dyes, as well as optical brighteners and fluorescent pigments may also be included in the golf ball covers produced with polymers formed according to the present invention. Such additional ingredients may be added in any amounts that will achieve their desired purpose.

Any method known to one of ordinary skill in the art may be used to polyurethanes of the present invention. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogeneous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition. Other methods suitable for forming the layers of the present invention include reaction injection molding ("RIM"), liquid injection molding ("LIM"), and pre-reacting the components to form an injection moldable thermoplastic polyurethane and then injection molding, all of which are known to one of ordinary skill in the art.

Additional components which can be added to the polyurethane composition include UV stabilizers and other dyes, as well as optical brighteners and fluorescent pigments and dyes. Such additional ingredients may be added in any amounts that will achieve their desired purpose. It has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the urethane elastomer material can be applied over the core using a variety of application techniques such as spraying, dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Pat. No. 5,733,428, the disclosure of which is hereby incorporated by reference in its entirety.

The outer cover is preferably formed around the inner cover by mixing and introducing the material in the mold halves. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing cores into the mold halves is determined to be

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approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using centering pins moving into holes in each mold. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity. After the reacting materials have resided in top mold halves for about 40 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture.

A ball cup holds the ball core through reduced pressure (or partial vacuum). Upon location of the coated core in the halves of the mold after gelling for about 40 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit, inverted and mated with other mold halves which, at an appropriate time earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

Similarly, U.S. Pat. No. 5,006,297 to Brown et al. and U.S. Pat. No. 5,334,673 to Wu both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. Further, U.S. Pat. Nos. 6,180,040 and 6,180,722 disclose methods of preparing dual core golf balls. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

Depending on the desired properties, balls prepared according to the invention can exhibit substantially the same or higher resilience, or coefficient of restitution ("COR"), with a decrease in compression or modulus, compared to balls of conventional construction. Additionally, balls prepared according to the invention can also exhibit substantially higher resilience, or COR, without an increase in compression, compared to balls of conventional construction. Another measure of this resilience is the "loss tangent," or $\tan \delta$, which is obtained when measuring the dynamic stiffness of an object. Loss tangent and terminology relating to such dynamic properties is typically described according to ASTM D4092-90. Thus, a lower loss tangent indicates a higher resiliency, thereby indicating a higher rebound capacity. Low loss tangent indicates that most of the energy imparted to a golf ball from the club is converted to dynamic energy, i.e., launch velocity and resulting longer distance. The rigidity or compressive stiffness of a golf ball may be measured, for example, by the dynamic stiffness. A higher dynamic stiffness indicates a higher compressive stiffness. To produce golf balls having a desirable compressive stiffness, the dynamic stiffness of the crosslinked reaction product material should be less than about 50,000 N/m at -50°C . Preferably, the dynamic stiffness should be between about 10,000 and 40,000 N/m at -50°C ., more preferably, the dynamic stiffness should be between about 20,000 and 30,000 N/m at -50°C .

The molding process and composition of golf ball portions typically results in a gradient of material properties. Methods employed in the prior art generally exploit hardness to quantify these gradients. Hardness is a qualitative measure of static modulus and does not represent the modulus of the material at the deformation rates associated with golf ball use, i.e., impact by a club. As is well known to one

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skilled in the art of polymer science, the time-temperature superposition principle may be used to emulate alternative deformation rates. For golf ball portions including polybutadiene, a 1-Hz oscillation at temperatures between 0° C. and -50° C. are believed to be qualitatively equivalent to golf ball impact rates. Therefore, measurement of loss tangent and dynamic stiffness at 0° C. to -50° C. may be used to accurately anticipate golf ball performance, preferably at temperatures between about -20° C. and -50° C.

Referring to FIG. 3, in another embodiment of the present invention, a golf ball 5 of the present invention is substantially spherical and has a cover 25 with a plurality of dimples 27 formed on the outer surface thereof.

Referring to FIGS. 4-6, the golf ball 5 includes an inner core 10, an outer core 15 and 20, and the cover 25 (shown without dimples). The inner core 10 includes a three-dimensional outer surface 28, a center C, a central portion 30, and a plurality of projections 35. The central portion 30 and projections 35 are integrally formed, so that the inner core is a single piece.

Referring to FIG. 6, the outer surface 28 of the inner core is defined by radial distances from the center C. At least two of the radial distances about the outer surface are different. The central portion 30 has a radius, designated by the arrow r_{cp} , that extends from the core center C to the outer surface of the central portion. The central portion 30 is solid in this embodiment.

Referring to FIGS. 5 and 6, each of the projections 35 extend radially outwardly from the central portion 30, and are spaced from one another to define gaps 40 there between. The projections 35 are shaped so that the inner core 10 is substantially spherically symmetrical.

Each projection 35 has an enlarged free end 45 and a substantially conical shape. Each free end 45 includes an open recess 50. Each projection has a radius, designated by the arrow r_p , that extends from the core center C to the outer surface 28 at the free end 45. The projection radii r_p differ from the central portion radius r_{cp} .

Referring to FIG. 5, each recess 50 is formed by three integral side walls 55. Each of the side walls 55 is shaped like a flat quarter circle. The quarter circle includes two straight edges 60 joined by a curved edge 65. In each projection 35, each of the side walls 55 is joined at the straight edges 60. The curved edges 65 of each of the projections allow the inner core to have a spherical shape.

With reference to a three-dimensional Cartesian Coordinate system, there are perpendicular x, y, and z axes, respectively that form eight octants. There are eight projections 35 with one in each octant of the coordinate system, so that each of the projections 35 forms an octant of the skeletal sphere. Thus, the inner core is symmetrical. The gaps 40 define three perpendicular concentric rings 70_x, 70_y, and 70_z. The subscript for the reference number 70 designates the central axis of the ring about which the ring circumscribes.

Turning to FIGS. 4 and 6, the outer core includes a first section 15 and a second section 20. The first section 15 fills the gaps 40 around the projections 35, and is disposed between the side walls 55 of adjacent projections 35. It is preferred that the diameter of the core which includes the inner core and the outer core is between about 1.00 inches and about 1.64 inches for a ball having a diameter of 1.68 inches.

The second section 20 fills the recesses 50 of each projection 35, and is disposed between the side walls 55 of a single projection 35. The outer core is formed so that the outer core terminates flush with the free end 45 of each projection 35. The outer core has a substantially spherical

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outer surface. The cover 25 is formed about the inner core 10 and the outer core sections 15 and 20, so that both the inner and outer cores abut the cover.

Referring to FIG. 4, the formation of a golf ball starts with forming the inner core 10. The inner core 10, outer core sections 15 and 20, and the cover 25 are formed by compression molding, by injection molding, or by casting. These methods of forming cores and covers of this type are well known in the art.

The materials used for the inner and outer core, as well as the cover, are selected so that the desired playing characteristics of the ball are achieved. The inner and outer core materials have substantially different material properties so that there is a predetermined relationship between the inner and outer core materials, to achieve the desired playing characteristics of the ball.

In one embodiment, the inner core is formed of a first material having a first Shore D hardness, a first elastic modulus, a first specific gravity, and a first Bashore resilience. The outer core is formed of a second material having a second Shore D hardness, a second elastic modulus, a second specific gravity, and a second Bashore resilience. Preferably, the material property of the first material equals at least one selected from the group consisting of the first Shore D hardness differing from the second Shore D hardness by at least 10 points, the first elastic modulus differing from the second elastic modulus by at least 10%, the first specific gravity differing from the second specific gravity by at least 0.1, or a first Bashore resilience differing from the second Bashore resilience by at least 10%. It is more preferred that the first material have all of these material property relationships.

Moreover, it is preferred that the first material has the first Shore D hardness between about 30 and about 80, the first elastic modulus between about 5,000 psi and about 100,000 psi, the first specific gravity between about 0.8 and about 1.6, and the first Bashore resilience greater than 30%.

In another embodiment, the first Shore D hardness is less than the second Shore D hardness, the first elastic modulus is less than the second elastic modulus, the first specific gravity is less than the second specific gravity, and the first Bashore resilience is less than the second Bashore resilience. In another embodiment, the first material properties are greater than the second material properties. The relationship between the first and second material properties depends on the desired playability characteristics.

Suitable inner and outer core materials include HNP's neutralized with organic fatty acids and salts thereof, metal cations, or a combination of both, thermosets, such as rubber, polybutadiene, polyisoprene; thermoplastics, such as ionomer resins, polyamides or polyesters; or thermoplastic elastomers. Suitable thermoplastic elastomers include PEBAX®, HYTREL®, thermoplastic urethane, and KRATON®, which are commercially available from Elf-Atochem, DuPont, BF Goodrich, and Shell, respectively. The inner and outer core materials can also be formed from a castable material. Suitable castable materials include, but are not limited to, urethane, urea, epoxy, diols, or curatives.

The cover 25 is selected from conventional materials used as golf ball covers based on the desired performance characteristics. The cover may be comprised of one or more layers. Cover materials such as ionomer resins, blends of ionomer resins, thermoplastic or thermoset urethanes, and balata, can be used as known in the art and discussed above.

Referring to FIG. 7, another embodiment of the golf ball 505 is shown. Similar structures to those discussed above use the same reference number preceded with the numeral

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"5." The golf ball **505** includes an outer core with a first section **515** and a second section **520**. The first section **515** and the second section **520** are formed of two materials with different material properties. In this embodiment, the core includes three different materials.

Referring to FIG. 8, another embodiment of the golf ball **605** is shown. Similar structures to those discussed above use the same reference number preceded with the numeral "6.") The golf ball **605** includes an intermediate layer **612** disposed between the cover **625** and the inner core **610** and outer cores **615** and **620**. The intermediate layer **612** is formed of either outer core material, cover material, or a different material. The first section **615** and the second section **620** of the outer core are formed of materials with the same material properties. However, in another embodiment, sections **615** and **620** can be formed of different materials. The intermediate layer **612** covers the inner core **610**, outer core **615** and **620**, and forms a continuous layer beneath the cover **625**.

Referring to FIG. 9, another embodiment of the golf ball **705** is shown. Similar structures to those discussed above use the same reference number preceded with the numeral "7." The golf ball **705** includes an intermediate layer **712** disposed between the cover **725** and the inner core **710** and outer cores **715** and **720**. The intermediate layer **712** is formed of either outer core material, cover material or a different material. The first section **715** and the second section **720** of the outer core are formed of materials with different material properties. The intermediate layer **712** covers the inner core **710**, outer core **715** and **720**, and forms a continuous layer beneath the cover **725**.

Referring to FIG. 10, another embodiment of the golf ball **805** is shown. Similar structures to those discussed above use the same reference number preceded with the numeral "8." The golf ball **805** includes an outer core with a multi-material first section **815a** and **815b** disposed within the gaps **840**. The different portions **815a**, **815b** of the first section of the outer core are formed of two materials with different material properties.

In other embodiments, additional layers may be added to those mentioned above or the existing layers may be formed by multiple materials.

Referring to FIG. 11, another embodiment of the golf ball **905** is shown. Similar structures to those discussed above use the same reference number preceded with the numeral "9." The golf ball **905** includes an inner core **910** including a central portion **930** and a plurality of outwardly radially extending projections **935**. The central portion **930** is hollow to define a chamber **990** therein. The outer core is formed from a first section **915** disposed within the gaps **940**, and a second section **920** disposed within the recesses **950**. The first section and the second section are formed of material with the same material properties. The cover section **925** surrounds the outer core **915** and **920**. The hollow central portion **930** reduces the volume of the inner core **910** material. The central portion may include a fluid.

Referring to FIG. 12, another embodiment of the golf ball **1005** is shown. Similar structures to those discussed above use the same reference number preceded with the numeral "10." The golf ball **1005** includes an inner core **1010** and an outer core **1015**, **1020**. The inner core **1010** includes a central portion **1030** and a plurality of outwardly radially extending projections **1035**. The central portion **1030** is hollow and surrounds a fluid-filled center **1095**. The fluid-filled center **1095** is formed of an envelope **1096** containing a fluid **1097**. The outer core is formed from a first section **1015** disposed within the gaps **1040**, and a second section

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1020 disposed within the recesses **1050**. The first section and the second section are formed of material with the same material properties. The cover material **1025** surrounds the inner and outer cores.

Referring to FIG. 12, when the core is formed with a fluid-filled center **1095**, the center is formed first then the inner core **1020** is molded around the center. Conventional molding techniques can be used for this operation. Then the outer core **1015**, **1020** and cover **1025** are formed thereon, as discussed above.

Referring to FIGS. 11 and 12, the fluid within the inner core can be a wide variety of materials including air, water solutions, liquids, gels, foams, hot-melts, other fluid materials and combinations thereof. The fluid is varied to modify the performance parameters of the ball, such as the moment of inertia or the spin decay rate.

Examples of suitable liquids include either solutions such as salt in water, corn syrup, salt in water and corn syrup, glycol and water or oils. The liquid can further include pastes, colloidal suspensions, such as clay, barytes, carbon black in water or other liquid, or salt in water/glycol mixtures. Examples of suitable gels include water gelatin gels, hydrogels, water/methyl cellulose gels and gels comprised of copolymer rubber based materials such as styrene-butadiene-styrene rubber and paraffinic and/or naphthenic oil. Examples of suitable melts include waxes and hot melts. Hot-melts are materials which at or about normal room temperatures are solid but at elevated temperatures become liquid. A high melting temperature is desirable since the liquid core is heated to high temperatures during the molding of the inner core, outer core, and the cover. The liquid can be a reactive liquid system, which combines to form a solid. Examples of suitable reactive liquids are silicate gels, agar gels, peroxide cured polyester resins, two part epoxy resin systems and peroxide cured liquid polybutadiene rubber compositions.

Referring to FIG. 13, another embodiment of an inner core **2010** is shown. The inner core **2010** includes a spherical central portion **2030** having an outer surface **2031**, and a plurality of projections **2035** extending radially outwardly from the central portion **2030**. The projections **2035** include a base **2036** adjacent the outer surface **2031** and a pointed free end **2038**. The projections **2035** are substantially conical and taper from the base **2036** to the pointed free end **2038**. It is preferred that the bases cover greater than about 15% of the outer surface. More preferably, the bases should cover greater than about 50% of the outer surface. Most preferably, the bases should be circular in shape and cover greater than about 80% of the outer surface and less than about 85%. As a result, the projections **2035** are spaced from one another and the area of the outer surface **2031** between each projection base **2036** is less than the area of each base. The projections **2035** are conical and configured so that the free ends **2038** of the projections form a spheroid. The base can have other shapes, such as polygons. Examples of polygon shapes that can be used for the base are triangles, pentagons, and hexagons. In addition, instead of the projections having a circular cross-section they can have other cross-sectional shapes such as square.

The projections further include a base diameter, designated by the letter d, and a projection height, designated by the letter h. It is preferred that the base diameter d is greater than or equal to the projection height h. This allows an included angle α between two diametrically opposed sides of the projection, designated L1 and L2, to be about 60° or more. More preferably the angle α is about 90° or more and

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most preferably the angle α is about 135° . This allows a simple mold to be used from which the core can be extracted.

To form a golf ball with inner core **2010** an outer core, as discussed above, is disposed around the inner core **2010** so that the outer core material is disposed within the gaps **2040** and the outer surface of the outer core is substantially spherical. The materials for the inner and outer cores are as discussed above. Then, the cover is formed thereon. The outer surface of the inner core has non-uniform radial distances from the center to various locations on the outer surface due to the conical projections **2035**.

Referring to FIG. 14, another embodiment of an inner core **3010** is shown. The inner core outer surface **3020** includes a plurality of projections **3035** formed so that gaps **3040** are formed surrounding each projection and between projections. Each projection includes a maximum length, which is the longest length of the projection, designated L. Each projection also includes a maximum width, which is the widest width of the projection, designated W. The surface of the projection is curved along the length L and width W. A substantial number of projections have the maximum length greater than the maximum width so that the projections are elongated. To form a golf ball, an outer core, as discussed above, is disposed around the inner core **3010** so that the outer core material is disposed within the gaps. The outer core material forms a substantially spherical surface. The materials for the inner and outer cores are as discussed above. Then a cover is formed thereon. The outer surface of the inner core has non-uniform radial distances from the center due to the projections and the indentations.

In this embodiment, in order to form the outer surface of this inner core, first, second and third surfaces are formed by rotation of a wave form about first, second and third axes, respectively. These axes are the x-, y- and z-axes in a Cartesian Coordinate System. The wave form used is sine wave. However, other wave forms can be used including, but not limited to, cosine or saw-tooth wave forms.

Referring to FIG. 15, an inner core **4010**, similar to that shown in FIG. 14, is illustrated. The inner core outer surface **4020** includes a plurality of projections **4035** formed so that gaps **4040** are formed surrounding each projection and between projections. Each projection includes a maximum length, which is the longest length of the projection, designated L. Each projection also includes a maximum width, which is the widest width of the projection, designated W. The surface of the projection is curved along the length L and width W. A substantial number of projections have the maximum length greater than the maximum width so that the projections are elongated.

In this embodiment, in order to form the outer surface of this inner core, the first, second, and third surfaces are formed as discussed above, and a fourth surface that is formed by rotating the wave form about a fourth axis that is about 45° from the first and second axes. The surface of the inner core **4020** is formed by the intersection of the first, second, third and fourth surfaces. Any number of surfaces greater than three can be used to create different outer surface geometries for the inner core. Furthermore, different axes can also be used.

In all the embodiments, there is a characteristic of the core that is called the "transition volume," which will now be discussed. Referring to FIG. 4, the ball **5** has a radius r_{IC} that includes only inner core material. The ball further an outer core and inner core radius r_{OIC} that includes both the inner core material and the outer core material. A transition radius is the outer core and inner core radius r_{OIC} less the inner

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core radius r_{IC} . The transition volume is the volume that is calculated when the transition radius is used. Thus, the transition volume is the volume of the golf ball that contains both inner core and outer core material therein, and it is an annular sector. The total volume of the core is the volume of all of the inner core material plus the volume of all of the outer core material. Favorable cores have been formed when the transition volume is at least 10% of the total core volume.

The "effective compression constant," which is designated EC, is the ratio of deflection of a 1.50 inch diameter sphere made of any single material used in the core under a 100 kg load that as represented by the formula $EC=F/d$, where, F is a 100 kg load; and d is the deflection in millimeters.

If the sphere tested is only inner core material, the effective compression constant for the inner core material alone is designated EC_{IC} . If the sphere tested is only outer core material, the effective compression constant for the outer core material alone is designated EC_{OC} . The sum of the constants for the inner core EC_{IC} and outer core EC_{OC} is the constant EC_S . If the sphere tested is inner and outer core material, the core effective compression constant is designated EC_C .

It has been determined that very favorable cores are formed when their core effective compression constant EC_C is less than the sum of the effective compression constants of the inner core and outer core EC_S . It is recommended that the core effective compression constant EC_C is less than about 90% of the sum of the effective compression constants of the inner core and outer core EC_S . More preferably, the core effective compression constant EC_C is less than or equal to about 50% of the sum of the effective compression constants of the inner core and outer core EC_S . The ratios of the inner core material to outer core material and the geometry of the inner core to the outer core are selected to achieve these core effective compression constants.

The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball cured polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D.

In addition to the HNP's neutralized with organic fatty acids and salts thereof, core compositions may comprise at least one rubber material having a resilience index of at least about 40. Preferably the resilience index is at least about 50. Polymers that produce resilient golf balls and, therefore, are suitable for the present invention, include but are not limited to CB23, CB22, commercially available from of Bayer Corp. of Orange, Tex., BR60, commercially available from Enichem of Italy, and 1207G, commercially available from Goodyear Corp. of Akron, Ohio.

Additionally, the unvulcanized rubber, such as polybutadiene, in golf balls prepared according to the invention typically has a Mooney viscosity of between about 40 and about 80, more preferably, between about 45 and about 65, and most preferably, between about 45 and about 55. Mooney viscosity is typically measured according to ASTM-D1646.

When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and

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more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 500 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-D2240, less than about 45 Shore D, preferably less than about 40 Shore D, more preferably between about 25 and about 40 Shore D, and most preferably between about 30 and about 40 Shore D. The casing preferably has a material hardness of less than about 70 Shore D, more preferably between about 30 and about 70 Shore D, and most preferably, between about 50 and about 65 Shore D.

In a preferred embodiment, the intermediate layer material hardness is between about 40 and about 70 Shore D and the outer cover layer material hardness is less than about 40 Shore D. In a more preferred embodiment, a ratio of the intermediate layer material hardness to the outer cover layer material hardness is greater than 1.5.

It should be understood, especially to one of ordinary skill in the art, that there is a fundamental difference between "material hardness" and "hardness, as measured directly on a golf ball." Material hardness is defined by the procedure set forth in ASTM-D2240 and generally involves measuring the hardness of a flat "slab" or "button" formed of the material of which the hardness is to be measured. Hardness, when measured directly on a golf ball (or other spherical surface) is a completely different measurement and, therefore, results in a different hardness value. This difference results from a number of factors including, but not limited to, ball construction (i.e., core type, number of core and/or cover layers, etc.), ball (or sphere) diameter, and the material composition of adjacent layers. It should also be understood that the two measurement techniques are not linearly related and, therefore, one hardness value cannot easily be correlated to the other.

In one embodiment, the core of the present invention has an Atti compression of between about 50 and about 90, more preferably, between about 60 and about 85, and most preferably, between about 65 and about 85. The overall outer diameter ("OD") of the core is less than about 1.590 inches, preferably, no greater than 1.580 inches, more preferably between about 1.540 inches and about 1.580 inches, and most preferably between about 1.525 inches to about 1.570 inches. The OD of the casing of the golf balls of the present invention is preferably between 1.580 inches and about 1.640 inches, more preferably between about 1.590 inches to about 1.630 inches, and most preferably between about 1.600 inches to about 1.630 inches.

The present multilayer golf ball can have an overall diameter of any size. Although the United States Golf Association ("USGA") specifications limit the minimum size of a competition golf ball to 1.680 inches. There is no specification as to the maximum diameter. Golf balls of any size, however, can be used for recreational play. The preferred diameter of the present golf balls is from about 1.680 inches to about 1.800 inches. The more preferred diameter is from about 1.680 inches to about 1.760 inches. The most preferred diameter is about 1.680 inches to about 1.740 inches.

The golf balls of the present invention should have a moment of inertia ("MOI") of less than about 85 and, preferably, less than about 83. The MOI is typically measured on model number MOI-005-104 Moment of Inertia Instrument manufactured by Inertia Dynamics of Collins-

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ville, Conn. The instrument is plugged into a PC for communication via a COMM port and is driven by MOI Instrument Software version #1.2.

U.S. Pat. Nos. 6,193,619; 6,207,784; and 6,221,960, and U.S. application Ser. No. 09/594,031, filed Jun. 15, 2000; Ser. No. 09/677,871, filed Oct. 3, 2000, and Ser. No. 09/447,652, filed Nov. 23, 1999, are incorporated in their entirety herein by express reference thereto.

The highly-neutralized polymers of the present invention may also be used in golf equipment, in particular, inserts for golf clubs, such as putters, irons, and woods, and in golf shoes and components thereof.

As used herein, the term "about," used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range.

The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended solely as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball comprising:

a core comprising a center and an outer core layer, the center comprising a thermoset polybutadiene rubber composition having a first hardness; and the outer core layer comprising a polymer comprised of an acid group fully-neutralized by an organic acid or a salt of the organic acid, and a cation source or a suitable base of the cation source; and having a second hardness; and an inner cover layer and an outer cover layer comprising ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, thermoplastic elastomers, polybutadiene rubber, balata, grafted metallocene-catalyzed polymers, non-grafted metallocene-catalyzed polymers, single-site polymers, high-crystalline acid polymers and their ionomers, polyurethanes, polyureas, polyurethane-ureas; polyurea-urethanes; or cationic ionomers;

wherein the first hardness is from about 50 Shore A to about 55 Shore D and first hardness is less than the second Shore D hardness by at least about 10 points.

2. The golf ball of claim 1, wherein the cation source is selected from a group consisting of metal cations of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, or aluminum.

3. The golf ball of claim 1, wherein the organic acid is selected from the group consisting of aliphatic organic acids, aromatic organic acids, saturated mono-functional organic acids, unsaturated mono-functional organic acids, and multi-unsaturated mono-functional organic acids.

4. The golf ball of claim 1, wherein the salt of organic acids comprise the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, calcium, stearic, behenic, erucic, oleic, linoleic, dimerized derivatives, and mixtures thereof.

5. The golf ball of claim 1, wherein the center has a first elastic modulus and the outer core layer has a second elastic modulus, and the first elastic modulus is less than the second elastic modulus by at least 10%.

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6. The golf ball of claim 1, wherein the cover layer is formed from a non-castable material, or is castable, injection molded, or compression molded over the core.

7. The golf ball of claim 1, wherein the polymer comprises ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, thermoplastic elastomers, polybutadiene rubber, balata, grafted metallocene-catalyzed polymers, non-grafted metallocene-catalyzed polymers, single-site polymers, high-crystalline acid polymers and their ionomers, cationic ionomers, and mixtures thereof.

8. The golf ball of claim 1, wherein the core has a diameter of about 1.53 inches or greater.

9. The golf ball of claim 8, wherein the core comprises two or more layers.

10. The golf ball of claim 1, wherein at least one of the inner cover or outer cover comprises a polyurethane material, a polyurea material, a polyurethane-urea hybrid material, or a polyurea-urethane hybrid material.

11. The golf ball of claim 1, wherein at least one of the inner cover or outer cover comprise a polymer comprising an acid group fully-neutralized by an organic acid or a salt, a cation source, or a suitable base thereof.

12. The golf ball of claim 1, wherein the inner cover layer has material hardness of at least about 60 Shore D and the outer cover layer has a material hardness of no greater than about 60 Shore D.

13. The golf ball of claim 1, wherein the outer cover layer has material hardness of at least about 60 Shore D and the inner cover layer has a material hardness of no greater than about 60 Shore D.

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14. The golf ball of claim 1, wherein the core compression is no greater than about 80.

15. The golf ball of claim 1, wherein the core further comprises an organosulfur or the metal salt thereof.

16. A golf ball comprising:

a core comprising a center and an outer core layer, the center comprising a thermoset polybutadiene rubber composition having a first hardness and a first elastic modulus; and the outer core layer comprising a polymer comprised of an acid group fully-neutralized by an organic acid or a salt of the organic acid, and a cation source or a suitable base of the cation source; and having a second hardness and a second elastic modulus; and

a cover layer comprising an inner cover layer and an outer cover layer, at least one of the inner or outer cover layers comprising ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, thermoplastic elastomers, polybutadiene rubber, balata, grafted metallocene-catalyzed polymers, non-grafted metallocene-catalyzed polymers, single-site polymers, high-crystalline acid polymers and their ionomers, polyurethanes, polyureas, polyurethane-ureas; polyurea-urethanes; or cationic ionomers;

wherein the first hardness is from about 50 Shore A to about 55 Shore D and first hardness is less than the second Shore D hardness by at least about 10 points; and the first elastic modulus is less than the second elastic modulus by at least 10%.

* * * * *

Exhibit B

US008025593B2

(12) **United States Patent**
Rajagopalan et al.(10) **Patent No.:** **US 8,025,593 B2**
(45) **Date of Patent:** **Sep. 27, 2011**(54) **MULTI-LAYER-CORE GOLF BALL HAVING
HIGHLY-NEUTRALIZED POLYMER OUTER
CORE LAYER**(75) Inventors: **Murali Rajagopalan**, South Dartmouth,
MA (US); **Michael J. Sullivan**,
Barrington, RI (US)(73) Assignee: **Acushnet Company**, Fairhaven, MA
(US)(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 495 days.(21) Appl. No.: **12/238,511**(22) Filed: **Sep. 26, 2008**(65) **Prior Publication Data**

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Related U.S. Application Data(63) Continuation-in-part of application No. 12/208,631,
filed on Sep. 11, 2008, which is a continuation of
application No. 11/347,456, filed on Feb. 3, 2006, now
Pat. No. 7,652,086, which is a continuation-in-part of
application No. 10/959,751, filed on Oct. 6, 2004, now
Pat. No. 7,230,045, which is a continuation-in-part of
application No. 10/360,233, filed on Feb. 6, 2003, now
Pat. No. 6,939,907, which is a continuation-in-part of
application No. 10/118,719, filed on Apr. 9, 2002, now
Pat. No. 6,756,436.(60) Provisional application No. 60/301,046, filed on Jun.
26, 2001.(51) **Int. Cl.**
A63B 37/04 (2006.01)(52) **U.S. Cl.** **473/373; 473/372; 473/374**(58) **Field of Classification Search** None
See application file for complete search history.(56) **References Cited****U.S. PATENT DOCUMENTS**

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Primary Examiner — Robert Sellers(74) *Attorney, Agent, or Firm* — William B. Lacy(57) **ABSTRACT**

A golf ball including an inner core layer formed from a thermoset rubber composition and having a first surface hardness; a thermoplastic outer core layer having a second surface hardness, an inner surface hardness, and being formed from a copolymer of ethylene and an α,β -unsaturated carboxylic acid, an organic acid or salt thereof, and sufficient cation source to fully-neutralize the acid groups of the copolymer; an inner cover layer; and an outer cover layer; wherein the first surface hardness is less than the second surface hardness by at least 5 Shore C and less than the inner surface hardness by at least 5 Shore C.

11 Claims, No Drawings

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MULTI-LAYER-CORE GOLF BALL HAVING HIGHLY-NEUTRALIZED POLYMER OUTER CORE LAYER

CROSS-REFERENCE TO RELATED APPLICATIONS

This application continuation-in-part of co-pending U.S. patent application Ser. No. 12/208,631, filed Sep. 11, 2008, which is a continuation of U.S. patent application Ser. No. 11/347,456, filed Feb. 3, 2006, which issued as U.S. Pat. No. 7,652,086, which is a continuation-in-part of U.S. patent application Ser. No. 10/959,751, filed Oct. 6, 2004, which issued as U.S. Pat. No. 7,230,045, which is a continuation-in-part of U.S. patent application Ser. No. 10/360,233, filed Feb. 6, 2003, which issued as U.S. Pat. No. 6,939,907, which is a continuation-in-part of U.S. patent application Ser. No. 10/118,719, filed Apr. 9, 2002, which issued as U.S. Pat. No. 6,756,436, which claims priority to U.S. Provisional Patent Application No. 60/301,046, filed Jun. 26, 2001, now abandoned.

FIELD OF THE INVENTION

The present invention is directed to golf ball compositions and, in particular, polymer compositions including highly-neutralized polymers and blends thereof.

BACKGROUND OF THE INVENTION

Conventional golf balls can be divided into two general classes: solid and wound. Solid golf balls include one-piece, two-piece (i.e., solid core and a cover), and multi-layer (i.e., solid core of one or more layers and/or a cover of one or more layers) golf balls. Wound golf balls typically include a solid, hollow, or fluid-filled center, surrounded by a tensioned elastomeric material, and a cover. It is also possible to surround a hollow or fluid-filled center with a plurality of solid layers. Solid balls have traditionally been considered longer and more durable than wound balls, but many solid constructions lack the "feel" provided by the wound construction.

More recently, by altering ball construction and composition, manufacturers have been able to vary a wide range of playing characteristics, such as compression, velocity, "feel," and spin, optimizing each or all for various playing abilities. In particular, a variety of core and cover layer(s) constructions, such as multi-layer balls having dual cover layers and/or dual core layers, have been investigated and now allow many non-wound balls to exhibit characteristics previously maintainable in a solid-construction golf ball. These golf ball layers are typically constructed with a number of polymeric compositions and blends, including polybutadiene rubber, polyurethanes, polyamides, and ethylene-based ionomers.

Ionomers, and in particular ethylene α,β -ethylenically unsaturated carboxylic acid copolymers or a melt processable ionomer thereof, are a preferred polymer for many golf ball layers. One problem encountered with the use of ionomers as stiff layers, however, is the unprocessability of the material as the percent of neutralization of the acid group increases. Ionomers are stiffened by increasing the amount of neutralization by a metal cation or a salt thereof. Once the percent of neutralization is greater than about 60% (depending on metal cation selected), the melt flow of the ionomer becomes too low and the ease of processability decreases or disappears altogether.

There is a need, therefore, for ionomer compositions that are neutralized at high percentages, but in a manner that still

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allows resultant polymer compositions to be processable. The present invention describes such compositions and their use in a variety of golf ball core and cover layers.

SUMMARY OF THE INVENTION

The present invention is directed to a golf ball comprising a center comprising a highly-neutralized thermoplastic copolymer of ethylene and an α,β -unsaturated carboxylic acid, the acid being 100% neutralized by a salt of an organic acid, a cation source, or a suitable base of the organic acid; a cover; and an intermediate layer disposed between the center and the cover; wherein the golf ball has a first coefficient of restitution of 0.81 or greater when measured at an incoming velocity of 125 ft/s; and a sphere resulting from a combination of the center and the intermediate layer has a compression of 60 or greater.

The cation source is typically a metal cation of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, and aluminum. Ideally, the salt of an organic acid includes an organic acid, such as aliphatic organic acids, aromatic organic acids, saturated mono- or multi-functional organic acids, unsaturated mono- or multi-functional organic acids, and multi-unsaturated mono- or multi-functional organic acids. The salt of an organic acid may include stearic acid, behenic acid, erucic acid, oleic acid, linoleic acid or dimerized derivatives thereof. The salt of an organic acid includes a cation, such as barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, and calcium.

The thermoplastic polymer comprises ionomeric copolymers and terpolymers, ionomer precursors, grafted metal-locene-catalyzed polymers, high-crystalline acid polymers and their ionomers, or cationic ionomers. Preferably, the cover is injection molded, cast, reaction injection molded, or compression molded over the core. In one embodiment, the cover comprises an inner cover layer and an outer cover layer, at least one of which comprises a polyurethane material, a polyurea material, a polyurethane-urea hybrid material, or a polyurea-urethane hybrid material.

The center typically has a diameter of 1.50 inches or less and the intermediate layer has a thickness of 0.090 inches or greater, preferably between 0.090 inches and 0.180 inches. The compression can be 80 or greater. Additionally, the golf ball should concurrently have a second coefficient of restitution of 0.76 or greater when measured at an incoming velocity of 160 ft/s.

The present invention is also directed to a golf ball comprising an innermost core, a cover, and an intermediate layer disposed between the innermost core and the cover, wherein the intermediate layer comprises a highly-neutralized thermoplastic copolymer of ethylene and an α,β -unsaturated carboxylic acid, the acid being 100% neutralized by a salt of an organic acid, a cation source, or a suitable base of the organic acid, and wherein a sphere resulting from a combination of the center and the intermediate layer has a compression of 60 or greater.

The intermediate layer should have a flexural modulus of 50,000 psi or greater, preferably from 60,000 psi to 150,000 psi. In one embodiment, the center has a diameter of from 0.80 inches to 1.40 inches and a compression of 30 or less, and the intermediate layer has flexural modulus of 50,000 psi to 70,000 psi and a thickness of 0.110 inches or greater, and the cover comprises thermoset polymer having a hardness of from 45 Shore D to 60 Shore D and a thickness from 0.020 inches to 0.040 inches. Additionally, the golf ball should

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concurrently have a coefficient of restitution of 0.76 or greater when measured at an incoming velocity of 160 ft/s.

Additionally, the present invention is also directed to a golf ball comprising an innermost core, a cover, and an intermediate layer disposed between the innermost core and the cover, wherein the core comprises a highly-neutralized thermoplastic copolymer of ethylene and an α,β -unsaturated carboxylic acid, the acid being 100% neutralized by a salt of an organic acid, a cation source, or a suitable base of the organic acid, and wherein a sphere resulting from a combination of the center and the intermediate layer has a compression of 60 or greater.

Preferably, the compression is 80 or greater. In one embodiment, the golf ball has a coefficient of restitution of 0.80 or greater when measured at an incoming velocity of 125 ft/s. The core should have a diameter of 1.500 inches or less and/or an intermediate layer having a thickness of 0.090 inches or greater. Preferably, the intermediate layer thickness is between 0.090 inches and 0.180 inches. In an alternative embodiment, the core has a compression of 60 or less. The intermediate layer should have a flexural modulus of 50,000 psi or greater. Also, the cover can be injection molded, cast, reaction injection molded, or compression molded over the core.

The present invention is further directed to a golf ball including an inner core layer formed from a thermoset rubber composition and having a first surface hardness; a thermoplastic outer core layer having a second surface hardness, an inner surface hardness, and being formed from a copolymer of ethylene and an α,β -unsaturated carboxylic acid, an organic acid or salt thereof, and sufficient cation source to fully-neutralize the acid groups of the copolymer; an inner cover layer; and an outer cover layer. The first surface hardness is preferably less than the second surface hardness by at least 5 Shore C and less than the inner surface hardness by at least 5 Shore C, more preferably at least 7 Shore C, most preferably at least 9 Shore C.

The present invention is also directed to a golf ball including an inner core layer formed from a first rubber composition and having a first surface hardness; an intermediate core layer formed from a second rubber composition; a thermoplastic outer core layer having a second surface hardness, an inner surface hardness, and including a copolymer of ethylene and an α,β -unsaturated carboxylic acid, an organic acid or salt thereof, and sufficient cation source to fully-neutralize the acid groups of the copolymer; an inner cover layer; and an outer cover layer. The first surface hardness is preferably less than the second surface hardness by at least 5 Shore C and less than the inner surface hardness by at least 5 Shore C, more preferably at least 7 Shore C, most preferably at least 9 Shore C.

In one embodiment, the inner core has a diameter of 0.80 inches to 1.40 inches and a compression of 30 or less, and the outer core layer has flexural modulus of 50,000 psi to 70,000 psi and a thickness of 0.110 inches or greater, and the outer cover layer comprises castable thermoset polyurethane or polyurea having a hardness of from 45 Shore D to 60 Shore D and a thickness from 0.020 inches to 0.040 inches.

In another embodiment, a core resulting from a combination of the inner core layer, the intermediate core layer, and the thermoplastic outer core layer has a compression of 60 or greater. Preferably the core has a diameter of 1.500 inches or less and the outer core layer has a thickness of 0.090 inches or greater. The inner core has a first elastic modulus and the outer core layer has a second elastic modulus less than the first; the inner core has a first specific gravity and the outer core layer has a second specific gravity less than the first; the inner core

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has a first Bashore resilience and the outer core layer has a second Bashore resilience less than the first; or the first surface hardness is less than the second surface hardness by at least 7 Shore C and less than the inner surface hardness by at least 7 Shore C.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to highly-neutralized polymers and blends thereof ("HNP") for the use in golf equipment, preferably in ball cores, intermediate layers, and/or covers. The acid moieties of the HNP's, typically ethylene-based ionomers, are preferably neutralized greater than about 70%, more preferably greater than about 90%, and most preferably at least about 100%. The HNP's can be also be blended with a second polymer component, which, if containing an acid group, may be neutralized in a conventional manner, by the organic fatty acids of the present invention, or both. The second polymer component, which may be partially or fully neutralized, preferably comprises ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, polyamides, polycarbonates, polyesters, polyurethanes, polyureas, thermoplastic elastomers, polybutadiene rubber, balata, metallocene-catalyzed polymers (grafted and non-grafted), single-site polymers, high-crystalline acid polymers, cationic ionomers, and the like. HNP polymers typically have a material hardness of between about 20 and about 80 Shore D, and a flexural modulus of between about 3,000 psi and about 200,000 psi.

In one embodiment of the present invention the HNP's are ionomers and/or their acid precursors that are preferably neutralized, either fully or partially, with organic acid copolymers or the salts thereof. The acid copolymers are preferably α -olefin, such as ethylene, C_{3-8} $\alpha\beta$ -ethylenically unsaturated carboxylic acid, such as acrylic and methacrylic acid, copolymers. They may optionally contain a softening monomer, such as alkyl acrylate and alkyl methacrylate, wherein the alkyl groups have from 1 to 8 carbon atoms.

The acid copolymers can be described as E/X/Y copolymers where E is ethylene, X is an α,β -ethylenically unsaturated carboxylic acid, and Y is a softening comonomer. In a preferred embodiment, X is acrylic or methacrylic acid and Y is a C_{1-8} alkyl acrylate or methacrylate ester. X is preferably present in an amount from about 1 to about 35 weight percent of the polymer, more preferably from about 5 to about 30 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer. Y is preferably present in an amount from about 0 to about 50 weight percent of the polymer, more preferably from about 5 to about 25 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer.

Specific acid-containing ethylene copolymers include, but are not limited to, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/methyl acrylate copolymers. The most preferred acid-containing ethylene copolymers are, eth-

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ylene/(meth) acrylic acid/n-butyl, acrylate, ethylene/(meth) acrylic acid/ethyl acrylate, and ethylene/(meth) acrylic acid/methyl acrylate copolymers.

Ionomers are typically neutralized with a metal cation, such as Li, Na, Mg, or Zn. It has been found that by adding sufficient organic acid or salt of organic acid, along with a suitable base, to the acid copolymer or ionomer, the ionomer can be neutralized without losing processability to a level much greater than for a metal cation alone. Preferably, the acid moieties are neutralized greater than about 80%, preferably from 90-100%, most preferably 100% without losing processability. This accomplished by melt-blending an ethylene $\alpha\beta$ -ethylenically unsaturated carboxylic acid copolymer, for example, with an organic acid or a salt of organic acid, and adding a sufficient amount of a cation source to increase the level of neutralization of all the acid moieties (including those in the acid copolymer and in the organic acid) to greater than 90%, (preferably greater than 100%).

The organic acids of the present invention are aliphatic, mono- or multi-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. The salts of organic acids of the present invention include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, salts of fatty acids, particularly stearic, bebenic, erucic, oleic, linoleic or dimerized derivatives thereof. It is preferred that the organic acids and salts of the present invention be relatively non-migratory (they do not bloom to the surface of the polymer under ambient temperatures) and non-volatile (they do not volatilize at temperatures required for melt-blending).

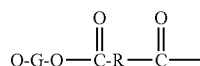
The ionomers of the invention may also be partially neutralized with metal cations. The acid moiety in the acid copolymer is neutralized about 1 to about 100%, preferably at least about 40 to about 100%, and more preferably at least about 90 to about 100%, to form an ionomer by a cation such as lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum, or a mixture thereof.

The acid copolymers of the present invention are prepared from 'direct' acid copolymers, copolymers polymerized by adding all monomers simultaneously, or by grafting of at least one acid-containing monomer onto an existing polymer. Other suitable highly-neutralized acid polymer compositions are disclosed in U.S. Patent Publication Nos. 2003/0114565 and 2005/0267240, and in U.S. patent application Ser. No. 11/270,066, which are incorporated herein, in their entirety, by reference.

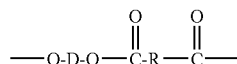
Thermoplastic polymer components, such as copolyetheresters, copolyesteresters, copolyetheramides, elastomeric polyolefins, styrene diene block copolymers and their hydrogenated derivatives, copolyesteramides, thermoplastic polyurethanes, such as copolyetherurethanes, copolyesterurethanes, copolyureurethanes, epoxy-based polyurethanes, polycaprolactone-based polyurethanes, polyureas, and polycarbonate-based polyurethanes fillers, and other ingredients, if included, can be blended in either before, during, or after the acid moieties are neutralized, thermoplastic polyurethanes.

The copolyetheresters are comprised of a multiplicity of recurring long chain units and short chain units joined head-to-tail through ester linkages, the long chain units being represented by the formula:

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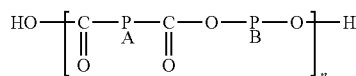


and the short chain units being represented by the formula:



where G is a divalent radical remaining after the removal of terminal hydroxyl groups from a poly (alkylene oxide) glycol having a molecular weight of about 400-8000 and a carbon to oxygen ratio of about 2.0-4.3; R is a divalent radical remaining after removal of hydroxyl groups from a diol having a molecular weight less than about 250; provided said short chain ester units amount to about 15-95 percent by weight of said copolyetherester. The preferred copolyetherester polymers are those where the polyether segment is obtained by polymerization of tetrahydrofuran and the polyester segment is obtained by polymerization of tetramethylene glycol and phthalic acid. For purposes of the invention, the molar ether: ester ratio can vary from 90:10 to 10:80; preferably 80:20 to 60:40; and the Shore D hardness is less than 70; preferably less than about 40.

The copolyetheramides are comprised of a linear and regular chain of rigid polyamide segments and flexible polyether segments, as represented by the general formula:



wherein PA is a linear saturated aliphatic polyamide sequence formed from a lactam or amino acid having a hydrocarbon chain containing 4 to 14 carbon atoms or from an aliphatic C_6 - C_8 diamine, in the presence of a chain-limiting aliphatic carboxylic diacid having 4-20 carbon atoms; said polyamide having an average molecular weight between 300 and 15,000; and PB is a polyoxyalkylene sequence formed from linear or branched aliphatic polyoxyalkylene glycols, mixtures thereof or copolyethers derived therefrom, said polyoxyalkylene glycols having a molecular weight of less than or equal to 6000; and n indicates a sufficient number of repeating units so that said polyetheramide copolymer has an intrinsic viscosity of from about 0.6 to about 2.05. The preparation of these polyetheramides comprises the step of reacting a dicarboxylic polyamide, the COOH groups of which are located at the chain ends, with a polyoxyalkylene glycol hydroxylated at the chain ends, in the presence of a catalyst such as a tetraalkyl ortho titanate having the general formula $\text{Ti}(\text{OR})_x$ wherein R is a linear branched aliphatic hydrocarbon radical having 1 to 24 carbon atoms. Again, the more polyether units incorporated into the copolyetheramide, the softer the polymer. The ether:amide ratios are as described above for the ether:ester ratios, as is the Shore D hardness.

The elastomeric polyolefins are polymers composed of ethylene and higher primary olefins such as propylene, hexene, octene, and optionally 1,4-hexadiene and or ethylidene norbornene or norbornadiene. The elastomeric polyolefins can be optionally functionalized with maleic anhydride, epoxy, hydroxy, amine, carboxylic acid, sulfonic acid, or thiol groups.

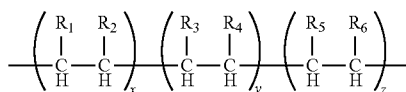
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Thermoplastic polyurethanes are linear or slightly chain branched polymers consisting of hard blocks and soft elastomeric blocks. They are produced by reacting soft hydroxy terminated elastomeric polyethers or polyesters with diisocyanates, such as methylene diisocyanate ("MDI"), p-phenylene diisocyanate ("PPDI"), or toluene diisocyanate ("TDI"). These polymers can be chain extended with glycols, secondary diamines, diacids, or amino alcohols. The reaction products of the isocyanates and the alcohols are called urethanes and these blocks are relatively hard and high melting. These hard high melting blocks are responsible for the thermoplastic nature of the polyurethanes.

Block styrene diene copolymers and their hydrogenated derivatives are composed of polystyrene units and polydiene units. They may also be functionalized with moieties such as OH, NH₂, epoxy, COOH, and anhydride groups. The polydiene units are derived from polybutadiene, polyisoprene units or copolymers of these two. In the case of the copolymer it is possible to hydrogenate the polyolefin to give a saturated rubbery backbone segments. These materials are usually referred to as SBS, SIS, or SEBS thermoplastic elastomers and they can also be functionalized with maleic anhydride.

Grafted metallocene-catalyzed polymers are also useful for blending with the HNP's of the present invention. The grafted metallocene-catalyzed polymers, while conventionally neutralized with metal cations, may also be neutralized, either partially for fully, with organic acids or salts thereof and an appropriate base. Grafted metallocene-catalyzed polymers useful, such as those disclosed in U.S. Pat. Nos. 5,703, 166; 5,824,746; 5,981,658; and 6,025,442, which are incorporated herein by reference, in the golf balls of the invention are available in experimental quantities from DuPont under the tradenames SURLYN® NMO 525D, SURLYN® NMO 524D, and SURLYN® NMO 499D, all formerly known as the FUSABOND® family of polymers, or may be obtained by subjecting a non-grafted metallocene-catalyzed polymer to a post-polymerization reaction to provide a grafted metallocene-catalyzed polymer with the desired pendant group or groups. Examples of metallocene-catalyzed polymers to which functional groups may be grafted for use in the invention include, but are not limited to, homopolymers of ethylene and copolymers of ethylene and a second olefin, preferably, propylene, butene, pentene, hexene, heptene, octene, and norbornene. Generally, the invention includes golf balls having at least one layer comprising at least one grafted metallocene-catalyzed polymer or polymer blend, where the grafted metallocene-catalyzed polymer is produced by grafting a functional group onto a metallocene-catalyzed polymer having the formula:



wherein R₁ is hydrogen, branched or straight chain alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl, carbocyclic, or aromatic; R₂ is hydrogen, lower alkyl including C₁-C₅, carbocyclic, or aromatic; R₃ is hydrogen, lower alkyl including C₁-C₅, carbocyclic, or aromatic; R₄ is selected from the group consisting of H, C_nH_{2n+1}, where n=1 to 18, and phenyl, in which from 0 to 5H within R₄ can be replaced by substituents COOH, SO₃H, NH₂, F, Cl, Br, I, OH, SH, silicone, lower alkyl esters and lower alkyl ethers, with the proviso that R₃ and R₄ can be combined to form a bicyclic ring; R₅ is hydrogen, lower alkyl including C₁-C₅, carbocyclic, or aromatic; R₆ is hydrogen, lower alkyl including C₁-C₅, carbocyclic, or aromatic; and wherein x, y and z are the relative percentages of each co-monomer. X can range from about 1 to 99 percent or more preferably from about 10 to about 70 percent and most preferred, from about 10 to 50 percent. Y can be from 99 to 1 percent, preferably, from 90 to 30 percent, or most preferably, 90 to 50 percent. Z can range from about 0 to about 49 percent. One of ordinary skill in the art would understand that if an acid moiety is present as a ligand in the above polymer that it may be neutralized up to 100% with an organic fatty acid as described above.

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Metallocene-catalyzed copolymers or terpolymers can be random or block and may be isotactic, syndiotactic, or atactic. The pendant groups creating the isotactic, syndiotactic, or atactic polymers are chosen to determine the interactions between the different polymer chains making up the resin to control the final properties of the resins used in golf ball covers, centers, or intermediate layers. As will be clear to those skilled in the art, grafted metallocene-catalyzed polymers useful in the invention that are formed from metallocene-catalyzed random or block copolymers or terpolymers will also be random or block copolymers or terpolymers, and will have the same tacticity of the metallocene-catalyzed polymer backbone.

As used herein, the term "phrase branched or straight chain alkyl" means any substituted or unsubstituted acyclic carbon-containing compounds. Examples of alkyl groups include lower alkyl, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl or t-butyl; upper alkyl, for example, octyl, nonyl, decyl, and the like; and lower alkylene, for example, ethylene, propylene, butylene, pentene, hexene, octene, norbornene, nonene, decene, and the like.

In addition, such alkyl groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Functional groups include, but are not limited to hydroxyl, amino, carboxyl, sulfonic amide, ester, ether, phosphates, thiol, nitro, silane and halogen (fluorine, chlorine, bromine and iodine), to mention but a few.

As used herein, the term "substituted and unsubstituted carbocyclic" means cyclic carbon-containing compounds, including, but not limited to cyclopentyl, cyclohexyl, cycloheptyl, and the like. Such cyclic groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups having from 1-28 carbon atoms. The cyclic groups of the invention may further comprise a heteroatom.

As mentioned above, R₁ and R₂ can also represent any combination of alkyl, carbocyclic or aryl groups, for example, 1-cyclohexylpropyl, benzyl cyclohexylmethyl, 2-cyclohexylpropyl, 2,2-methylcyclohexylpropyl, 2,2-methylphenylpropyl, and 2,2-methylphenylbutyl.

Non-grafted metallocene-catalyzed polymers useful in the present invention are commercially available under the trade name AFFINITY® polyolefin plastomers and ENGAGE® polyolefin elastomers commercially available from Dow Chemical Company and DuPont-Dow. Other commercially available metallocene-catalyzed polymers can be used, such as EXACT®, commercially available from Exxon and INSIGHT®, commercially available from Dow. The EXACT® and INSIGHT® line of polymers also have novel rheological behavior in addition to their other properties as a

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result of using a metallocene catalyst technology. Metallocene-catalyzed polymers are also readily available from Sentinel Products Corporation of Hyannis, Mass., as foamed sheets for compression molding.

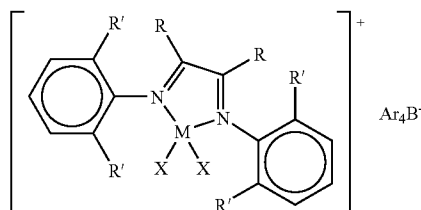
Monomers useful in the present invention include, but are not limited to, olefinic monomers having, as a functional group, sulfonic acid, sulfonic acid derivatives, such as chlorosulfonic acid, vinyl ethers, vinyl esters, primary, secondary, and tertiary amines, mono-carboxylic acids, dicarboxylic acids, partially or fully ester-derivatized mono-carboxylic and dicarboxylic acids, anhydrides of dicarboxylic acids, and cyclic imides of dicarboxylic acids.

In addition, metallocene-catalyzed polymers may also be functionalized by sulfonation, carboxylation, or the addition of an amine or hydroxy group. Metallocene-catalyzed polymers functionalized by sulfonation, carboxylation, or the addition of a hydroxy group may be converted to anionic ionomers by treatment with a base. Similarly, metallocene-catalyzed polymers functionalized by the addition of an amine may be converted to cationic ionomers by treatment with an alkyl halide, acid, or acid derivative.

The most preferred monomer is maleic anhydride, which, once attached to the metallocene-catalyzed polymer by the post-polymerization reaction, may be further subjected to a reaction to form a grafted metallocene-catalyzed polymer containing other pendant or functional groups. For example, reaction with water will convert the anhydride to a dicarboxylic acid; reaction with ammonia, alkyl, or aromatic amine forms an amide; reaction with an alcohol results in the formation of an ester; and reaction with base results in the formation of an anionic ionomer.

The HNP's of the present invention may also be blended with single-site and metallocene catalysts and polymers formed therefrom. As used herein, the term "single-site catalyst," such as those disclosed in U.S. Pat. No. 6,150,462 which is incorporated herein by reference, refers to a catalyst that contains an ancillary ligand that influences the steric and electronic characteristics of the polymerizing site in a manner that prevents formation of secondary polymerizing species. The term "metallocene catalyst" refers to a single-site catalyst wherein the ancillary ligands are comprising substituted or unsubstituted cyclopentadienyl groups, and the term "non-metallocene catalyst" refers to a single-site catalyst other than a metallocene catalyst.

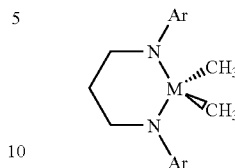
Non-metallocene single-site catalysts include, but are not limited to, the Brookhart catalyst, which has the following structure:



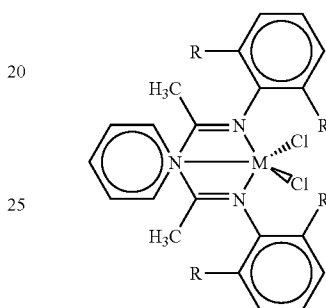
wherein M is nickel or palladium; R and R' are independently hydrogen, hydrocarbyl, or substituted hydrocarbyl; Ar is

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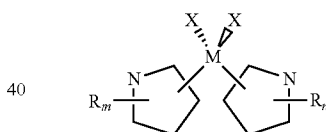
$(\text{CF}_3)_2\text{C}_6\text{H}_3$, and X is alkyl, methyl, hydride, or halide; the McConville catalyst, which has the structure:



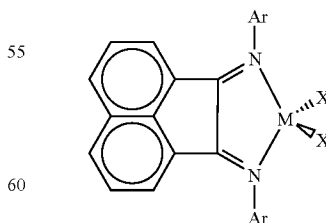
wherein M is titanium or zirconium. Iron (II) and cobalt (II) complexes with 2,6-bis(imino) pyridyl ligands, which have the structure:



where M is the metal, and R is hydrogen, alkyl, or hydrocarbyl. Titanium or zirconium complexes with pyrroles as ligands also serve as single-site catalysts. These complexes have the structure:



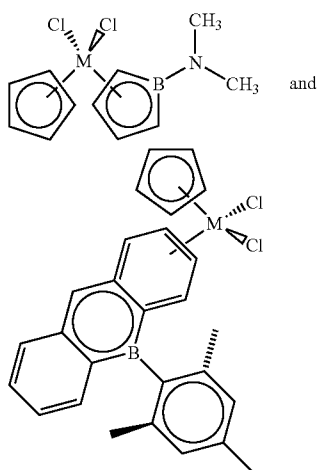
where M is the metal atom; m and n are independently 1 to 4, and indicate the number of substituent groups attached to the aromatic rings; R_m and R_n are independently hydrogen or alkyl; and X is halide or alkyl. Other examples include diimide complexes of nickel and palladium, which have the structure:



where Ar is aromatic, M is the metal, and X is halide or alkyl. Boratabenzene complexes of the Group IV or V metals also function as single-site catalysts. These complexes have the structure:

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where B is boron and M is the metal atom.

As used herein, the term “single-site catalyzed polymer” refers to any polymer, copolymer, or terpolymer, and, in particular, any polyolefin polymerized using a single-site catalyst. The term “non-metallocene single-site catalyzed polymer” refers to any polymer, copolymer, or terpolymer, and, in particular, any polyolefin polymerized using a single-site catalyst other than a metallocene-catalyst. The catalysts discussed above are examples of non-metallocene single-site catalysts. The term “metallocene catalyzed polymer” refers to any polymer, copolymer, or terpolymer, and, in particular, any polyolefin, polymerized using a metallocene catalyst.

As used herein, the term “single-site catalyzed polymer blend” refers to any blend of a single-site catalyzed polymer and any other type of polymer, preferably an ionomer, as well as any blend of a single-site catalyzed polymer with another single-site catalyzed polymer, including, but not limited to, a metallocene-catalyzed polymer.

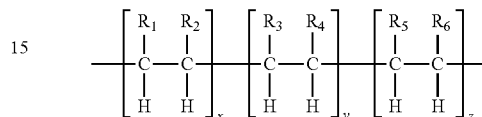
The terms “grafted single-site catalyzed polymer” and “grafted single-site catalyzed polymer blend” refer to any single-site catalyzed polymer or single-site catalyzed polymer blend in which the single-site catalyzed polymer has been subjected to a post-polymerization reaction to graft at least one functional group onto the single-site catalyzed polymer. A “post-polymerization reaction” is any reaction that occurs after the formation of the polymer by a polymerization reaction.

The single-site catalyzed polymer, which may be grafted, may also be blended with polymers, such as non-grafted single-site catalyzed polymers, grafted single-site catalyzed polymers, ionomers, and thermoplastic elastomers. Preferably, the single-site catalyzed polymer is blended with at least one ionomer of the present invention.

Grafted single-site catalyzed polymers useful in the golf balls of the invention may be obtained by subjecting a non-grafted single-site catalyzed polymer to a post-polymerization reaction to provide a grafted single-site catalyzed polymer with the desired pendant group or groups. Examples of single-site catalyzed polymers to which functional groups may be grafted for use in the invention include, but are not limited to, homopolymers of ethylene and propylene and copolymers of ethylene and a second olefin, preferably, propylene, butene, pentene, hexene, heptene, octene, and norbornene. Monomers useful in the present invention include, but are not limited to olefinic monomers having as a functional group sulfonic acid, sulfonic acid derivatives, such as

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chlorosulfonic acid, vinyl ethers, vinyl esters, primary, secondary, and tertiary amines, epoxies, isocyanates, mono-carboxylic acids, dicarboxylic acids, partially or fully ester derivatized mono-carboxylic and dicarboxylic acids, anhydrides of dicarboxylic acids, and cyclic imides of dicarboxylic acids. Generally, this embodiment of the invention includes golf balls having at least one layer comprising at least one grafted single-site catalyzed polymer or polymer blend, where the grafted single-site catalyzed polymer is produced by grafting a functional group onto a single-site catalyzed polymer having the formula:



where R is hydrogen, branched or straight chain alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl, carbocyclic, aromatic or heterocyclic; R₂, R₃, R₅, and R₆ are hydrogen, lower alkyl including C₁-C₅, carbocyclic, aromatic or heterocyclic; R₄ is H, C_nH_{2n+1}, where n=1 to 18, and phenyl, in which from 0 to 5H within R₄ can be replaced by substituents such as COOH, SO₃H, NH₂, F, Cl, Br, I, OH, SH, epoxy, isocyanate, silicone, lower alkyl esters and lower alkyl ethers; also, R₃ and R₄ can be combined to form a bicyclic ring; and x, y and z are the relative percentages of each co-monomer. X can range from about 1 to about 100 percent or more preferably from 1 to 70 percent and most preferred, from about 1 to about 50 percent. Y can be from about 99 to about 0 percent, preferably, from about 9 to about 30 percent, or most preferably, about 9 to about 50 percent. Z can range from about 0 to about 50 percent. One of ordinary skill in the art would also understand that if an acid group is selected as a ligand in the above structure that it too could be neutralized with the organic fatty acids described above.

The HNP's of the present invention may also be blended with high crystalline acid copolymers and their ionomer derivatives (which may be neutralized with conventional metal cations or the organic fatty acids and salts thereof) or a blend of a high crystalline acid copolymer and its ionomer derivatives and at least one additional material, preferably an acid copolymer and its ionomer derivatives. As used herein, the term “high crystalline acid copolymer” is defined as a “product-by-process” in which an acid copolymer or its ionomer derivatives formed from a ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to 200° C., at pressures greater than about 20,000 psi preferably greater than about 25,000 psi, more pref. from about 25,000 psi to about 50,000 psi, wherein up to about 70 percent, preferably 100 percent, of the acid groups are neutralized with a metal ion, organic fatty acids and salts thereof, or a mixture thereof. The copolymer can have a melt index (“MI”) of from about 20 to about 300 g/10 min, preferably about 20 to about 200 g/10 min, and upon neutralization of the copolymer, the resulting acid copolymer and its ionomer derivatives should have an MI of from about 0.1 to about 30.0 g/10 min.

Suitable high crystalline acid copolymer and its ionomer derivatives compositions and methods for making them are disclosed in U.S. Pat. No. 5,580,927, the disclosure of which is hereby incorporated by reference in its entirety.

The high crystalline acid copolymer or its ionomer derivatives employed in the present invention are preferably formed

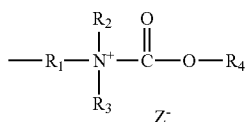
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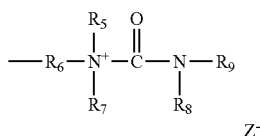
from a copolymer containing about 5 to about 35 percent, more preferably from about 9 to about 18, most preferably about 10 to about 13 percent, by weight of acrylic acid, wherein up to about 75 percent, most preferably about 60 percent, of the acid groups are neutralized with an organic fatty acid, salt thereof, or a metal ion, such as sodium, lithium, magnesium, or zinc ion.

Generally speaking, high crystalline acid copolymer and its ionomer derivatives are formed by polymerization of their base copolymers at lower temperatures, but at equivalent pressures to those used for forming a conventional acid copolymer and its ionomer derivatives. Conventional acid copolymers are typically polymerized at a polymerization temperature of from at least about 200° C. to about 270° C., preferably about 220° C., and at pressures of from about 23,000 to about 30,000 psi. In comparison, the high crystalline acid copolymer and its ionomer derivatives employed in the present invention are produced from acid copolymers that are polymerized at a polymerization temperature of less than 200° C., and preferably from about 130° C. to about 200° C., and at pressures from about 20,000 to about 50,000 psi.

The HNP's of the present invention may also be blended with cationic ionomers, such as those disclosed in U.S. Pat. No. 6,193,619 which is incorporated herein by reference. In particular, cationic ionomers have a structure according to the formula:



or the formula:



wherein R₁-R₉ are organic moieties of linear or branched chain alkyl, carbocyclic, or aryl; and Z is the negatively charged conjugate ion produced following alkylation and/or quaternization. The cationic polymers may also be quaternized up to 100% by the organic fatty acids described above.

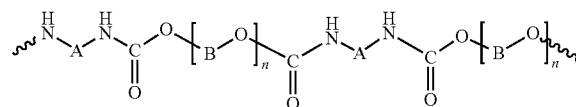
In addition, such alkyl group may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Functional groups include but are not limited to hydroxyl, amino, carboxyl, amide, ester, ether, sulfonic, siloxane, siloxyl, silanes, sulfonyl, and halogen.

As used herein, substituted and unsubstituted carbocyclic groups of up to about 20 carbon atoms means cyclic carbon-containing compounds, including but not limited to cyclopentyl, cyclohexyl, cycloheptyl, and the like. Such cyclic groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups as described above. The cyclic groups of the invention may further comprise a heteroatom.

The HNP's of the present invention may also be blended with polyurethane and polyurea ionomers which include

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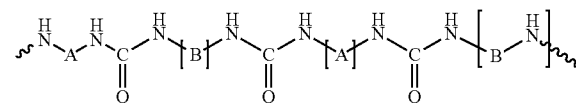
anionic moieties or groups, such as those disclosed in U.S. Pat. No. 6,207,784 which is incorporated herein by reference. Typically, such groups are incorporated onto the diisocyanate or diisocyanate component of the polyurethane or polyurea ionomers. The anionic group can also be attached to the polyol or amine component of the polyurethane or polyurea, respectively. Preferably, the anionic group is based on a sulfonic, carboxylic or phosphoric acid group. Also, more than one type of anionic group can be incorporated into the polyurethane or polyurea. Examples of anionic polyurethane ionomers with anionic groups attached to the diisocyanate moiety can have a chemical structure according to the following formula:



where A=R—Z⁻M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻ or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIIA, VIIB, VIIIB or VIIIB metal; x=1 to 5; B is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; and n=1 to 100. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x} or Hf^{+x}.

Exemplary anionic polyurethane ionomers with anionic groups attached to the polyol component of the polyurethane are characterized by the above chemical structure where A is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; B=R—Z⁻M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻ or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIIA, VIIB, VIIIB or VIIIB metal; x=1 to 5; and n=1 to 100. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x} or Hf^{+x}.

Examples of suitable anionic polyurea ionomers with anionic groups attached to the diisocyanate component have a chemical structure according to the following chemical structure:



where A=R—Z⁻M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻ or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIIA, VIIB, VIIIB or VIIIB metal; x=1 to 5; and B is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x} or Hf^{+x}.

Suitable anionic polyurea ionomers with anionic groups attached to the amine component of the polyurea are charac-

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terized by the above chemical structure where A is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; B=R—Z—M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻ or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIIA, VIIB, VIIB or VIIIB metal; and x=1 to 5. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x} or Hf^{+x}. The anionic polyurethane and polyurea ionomers may also be neutralized up to 100% by the organic fatty acids described above.

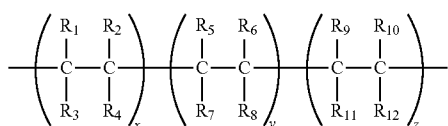
The anionic polymers useful in the present invention, such as those disclosed in U.S. Pat. No. 6,221,960 which is incorporated herein by reference, include any homopolymer, copolymer or terpolymer having neutralizable hydroxyl and/or dealkylable ether groups, and in which at least a portion of the neutralizable or dealkylable groups are neutralized or dealkylated with a metal ion.

As used herein "neutralizable" or "dealkylable" groups refer to a hydroxyl or ether group pendent from the polymer chain and capable of being neutralized or dealkylated by a metal ion, preferably a metal ion base. These neutralized polymers have improved properties critical to golf ball performance, such as resiliency, impact strength and toughness and abrasion resistance. Suitable metal bases are ionic compounds comprising a metal cation and a basic anion. Examples of such bases include hydroxides, carbonates, acetates, oxides, sulfides, and the like.

The particular base to be used depends upon the nature of the hydroxyl or ether compound to be neutralized or dealkylated, and is readily determined by one skilled in the art. Preferred anionic bases include hydroxides, carbonates, oxides and acetates.

The metal ion can be any metal ion which forms an ionic compound with the anionic base. The metal is not particularly limited, and includes alkali metals, preferably lithium, sodium or potassium; alkaline earth metals, preferably magnesium or calcium; transition metals, preferably titanium, zirconium, or zinc; and Group III and IV metals. The metal ion can have a +1 to +5 charge. Most preferably, the metal is lithium, sodium, potassium, zinc, magnesium, titanium, tungsten, or calcium, and the base is hydroxide, carbonate or acetate.

The anionic polymers useful in the present invention include those which contain neutralizable hydroxyl and/or dealkylable ether groups. Exemplary polymers include ethylene vinyl alcohol copolymers, polyvinyl alcohol, polyvinyl acetate, poly(p-hydroxymethylene styrene), and p-methoxy styrene, to name but a few. It will be apparent to one skilled in the art that many such polymers exist and thus can be used in the compositions of the invention. In general, the anionic polymer can be described by the chemical structure:



where R₁ is OH, OC(O)R_a, O-M^{+V}, (CH₂)_nR_b, (CHR_z)_nR_b, or aryl, wherein n is at least 1, R_a is a lower alkyl, M is a metal ion, V is an integer from 1 to 5, R_b is OH, OC(O)R_a, O-M^{+V}, and R_z is a lower alkyl or aryl, and R₂, R₃ and R₄ are each

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independently hydrogen, straight-chain or branched-chain lower alkyl. R₂, R₃ and R₄ may also be similarly substituted. Preferably n is from 1 to 12, more preferably 1 to 4.

The term "substituted," as used herein, means one or more hydrogen atoms has been replaced by a functional group. Functional groups include, but are not limited to, hydroxyl, amino, carboxyl, sulfonic, amide, ether, ether, phosphates, thiol, nitro, silane, and halogen, as well as many others which are quite familiar to those of ordinary skill in this art.

The terms "alkyl" or "lower alkyl," as used herein, includes a group of from about 1 to 30 carbon atoms, preferably 1 to 10 carbon atoms.

In the anionic polymers useful in the present invention, at least a portion of the neutralizable or dealkylable groups of R₁ are neutralized or dealkylated by an organic fatty acid, a salt thereof, a metal base, or a mixture thereof to form the corresponding anionic moiety. The portion of the neutralizable or dealkylable groups which are neutralized or dealkylated can be between about 1 to about 100 weight percent, preferably between about 50 to about 100 weight percent, more preferably before about 90 to about 100.

Neutralization or dealkylation may be performed by melting the polymer first, then adding a metal ion in an extruder. The degree of neutralization or dealkylation is controlled by varying the amount of metal ion added. Any method of neutralization or dealkylation available to those of ordinary skill in the art may also be suitably employed.

In one embodiment, the anionic polymer is repeating units any one of the three homopolymer units in the chemical structure above. In a preferred embodiment, R₂, R₃ and R₄ are hydrogen, and R₁ is hydroxyl, i.e., the anionic polymer is a polyvinyl alcohol homopolymer in which a portion of the hydroxyl groups have been neutralized with a metal base. In another preferred embodiment, R₂, R₃ and R₄ are hydrogen, R₁ is OC(O)R_a, and R_a is methyl, i.e., the anionic polymer is a polyvinyl acetate homopolymer in which a portion of the methyl ether groups have been dealkylated with a metal ion.

The anionic polymer can also be a copolymer of two different repeating units having different substituents, or a terpolymer of three different repeating units described in the above formula. In this embodiment, the polymer can be a random copolymer, an alternating copolymer, or a block copolymer, where the term "copolymer" includes terpolymers.

In another embodiment, the anionic polymer is a copolymer, wherein R₅, R₆, R₇ and R₈ are each independently selected from the group defined above for R₂. The first unit of the copolymer can comprise from about 1 to 99 percent weight percent of the polymer, preferably from about 5 to 50 weight percent, and the second unit of the copolymer can comprise from about 99 to 1 weight percent, preferably from about 95 to 50 weight percent. In one preferred embodiment, the anionic polymer is a random, alternating or block copolymer of units (Ia) and (Ib) wherein R₁ is hydroxyl, and each of the remaining R groups is hydrogen, i.e., the polymer is a copolymer of ethylene and vinyl alcohol. In another preferred embodiment, the anionic polymer is a random, alternating or block copolymer of units (Ia) and (Ib) wherein R₁ is OC(O)R₅, where R₅ is methyl, and each of the remaining R groups is hydrogen, i.e., the polymer is a copolymer of ethylene and vinyl acetate.

In another embodiment, the anionic polymer is an anionic polymer having neutralizable hydroxyl and/or dealkylable ether groups of as in the above chemical structure wherein R₁₋₉ and R₆ and R_z are as defined above; R₁₀₋₁₁ are each independently selected from the group as defined above for R₂; and R₁₂ is OH or OC(O)R₁₃, where R₁₃ is a lower alkyl;

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wherein x, y and z indicate relative weight percent of the different units. X can be from about 99 to about 50 weight percent of the polymer, y can be from about 1 to about 50 weight percent of the polymer, and z ranges from about 0 to about 50 weight percent of the polymer. At least a portion of the neutralizable groups R_1 are neutralized. When the amount of z is greater than zero, a portion of the groups R_{10} can also be fully or partially neutralized, as desired.

In particular, the anionic polymers and blends thereof can comprise compatible blends of anionic polymers and ionomers, such as the ionomers described above, and ethylene acrylic methacrylic acid ionomers, and their terpolymers, sold commercially under the trade names SURLYN® and IOTEK® by DuPont and Exxon respectively. The anionic polymer blends useful in the golf balls of the invention can also include other polymers, such as polyvinylalcohol, copolymers of ethylene and vinyl alcohol, poly(ethylethylene), poly(heptylethylene), poly(hexyldecylethylene), poly(isopentylethylene), poly(butyl acrylate), acrylate, poly(2-ethylbutyl acrylate), poly(heptyl acrylate), poly(2-methylbutyl acrylate), poly(3-methylbutyl acrylate), poly(N-octadecylacrylamide), poly(octadecyl methacrylate), poly(butoxyethylene), poly(methoxyethylene), poly(pentyloxyethylene), poly(1,1-dichloroethylene), poly(4-[(2-butoxyethoxy)methyl]styrene), poly[oxy(ethoxymethyl)ethylene], poly(oxyethylethylene), poly(oxytetramethylene), poly(oxytrimethylene), poly(silanes) and poly(silazanes), polyamides, polycarbonates, polyesters, styrene block copolymers, polyetheramides, polyurethanes, main-chain heterocyclic polymers and poly(furan tetracarboxylic acid diimides), as well as the classes of polymers to which they belong.

The anionic polymer compositions of the present invention typically have a flexural modulus of from about 500 psi to about 300,000 psi, preferably from about 2000 to about 200,000 psi. The anionic polymer compositions typically have a material hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D. The loss tangent, or dissipation factor, is a ratio of the loss modulus over the dynamic shear storage modulus, and is typically less than about 1, preferably less than about 0.01, and more preferably less than about 0.001 for the anionic polymer compositions measured at about 23° C. The specific gravity is typically greater than about 0.7, preferably greater than about 1, for the anionic polymer compositions. The dynamic shear storage modulus, or storage modulus, of the anionic polymer compositions at about 23° C. is typically at least about 10,000 dyn/cm².

The golf balls of the present invention may comprise a variety of constructions. In one embodiment of the present invention, golf ball includes a core, an inner cover layer surrounding the core, and an outer cover layer. Preferably, the core is solid. More preferably, the core is a solid, single-layer core. In a preferred embodiment, the solid core comprises the HNP's of the present invention. In an alternative embodiment, the solid core may include compositions having a base rubber, a crosslinking agent, a filler, and a co-crosslinking or initiator agent, and the inner cover layer comprises the HNP's of the present invention.

The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene having a cis-structure of at least 40%. More preferably, the base rubber comprises high-Mooney-viscosity rubber. If desired, the polybutadiene can also be mixed with other elastomers

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known in the art such as natural rubber, polyisoprene rubber and/or styrene-butadiene rubber in order to modify the properties of the core.

The crosslinking agent includes a metal salt of an unsaturated fatty acid such as a zinc salt or a magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms such as acrylic or methacrylic acid. Suitable cross linking agents include metal salt diacrylates, dimethacrylates and monomethacrylates wherein the metal is magnesium, calcium, zinc, aluminum, sodium, lithium or nickel. The crosslinking agent is present in an amount from about 15 to about 40 parts per hundred of the rubber, preferably in an amount from about 19 to about 25 parts per hundred of the rubber and most preferably having about 20 to 24 parts crosslinking agent per hundred of rubber. The core compositions of the present invention may also include at least one organic or inorganic cis-trans catalyst to convert a portion of the cis-isomer of polybutadiene to the trans-isomer, as desired.

The initiator agent can be any known polymerization initiator which decomposes during the cure cycle. Suitable initiators include peroxide compounds such as dicumyl peroxide, 1,1-di-(t-butylperoxy) 3,3,5-trimethyl cyclohexane, a-a bis-(t-butylperoxy)diisopropylbenzene, 2,5-dimethyl-2,5 di-(t-butylperoxy)hexane or di-t-butyl peroxide and mixtures thereof.

Fillers, any compound or composition that can be used to vary the density and other properties of the core, typically include materials such as tungsten, zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate, metals, metal oxides and salts, regrind (recycled core material typically ground to about 30 mesh particle), high-Mooney-viscosity rubber regrind, and the like.

The HNP compositions of the present invention may also be moisture resistant. For purposes of the present disclosure, a composition is "moisture resistant" if it has a moisture vapor transmission rate ("MVTR") of 12.5 gml/100 in²/day or less. Preferably, the moisture resistant compositions of the present invention have an MVTR of 8.0 gml/100 in²/day or less, or 6.5 gml/100 in²/day or less, or 5.0 gml/100 in²/day or less, or 4.0 gml/100 in²/day or less, or 2.5 gml/100 in²/day or less, or 2.0 gml/100 in²/day or less. As used herein, moisture vapor transmission rate (MVTR) is given in gml/100 in²/day, and is measured at 20° C., and according to ASTM F1249-99.

In a particular embodiment, the cation source is selected from metal ions and compounds of calcium, metal ions and compounds of zinc, and combinations thereof. In a particular aspect of this embodiment, the equivalent percentage of calcium and/or zinc salt(s) in the final composition is 50% or higher, or 60% or higher, or 70% or higher, or 80% or higher, or 90% or higher, based on the total salts present in the final composition, wherein the equivalent % is determined by multiplying the mol % of the cation by the valence of the cation. In another particular embodiment, the cation source is selected from metal ions and compounds of lithium, sodium, potassium, magnesium, calcium, zinc, and combinations thereof. In another particular embodiment, the cation source is selected from metal ions and compounds of lithium, metal ions and compounds of zinc, and combinations thereof. Suitable cation sources also include mixtures of lithium and/or zinc cations with other cations. Other cations suitable for mixing with lithium and/or zinc cations to produce the HNP include, but are not limited to, the "less hydrophilic" cations disclosed in U.S. Patent Application Publication No. 2006/0106175; conventional HNP cations, such as those disclosed in U.S. Pat. Nos. 6,756,436 and 6,824,477; and the cations disclosed in U.S. Patent Application Publication No. 2005/

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0267240. The entire disclosure of each of these references is hereby incorporated herein by reference. In a particular aspect of this embodiment, the percentage of lithium and/or zinc salts in the composition is preferably 50% or higher, or 55% or higher, or 60% or higher, or 65% or higher, or 70% or higher, or 80% or higher, or 90% or higher, or 95% or higher, or 100%, based on the total salts present in the composition. The amount of cation source used is readily determined based on the desired level of neutralization.

The golf ball cores of the present invention may also comprise a variety of constructions. For example, the core may comprise a single layer or a plurality of layers. The core may also comprise a layer of tensioned elastomeric material. In another embodiment of the present invention, golf ball comprises a solid center surrounded by at least one additional solid outer core layer. The "dual" core is surrounded by a "double" cover comprising an inner cover layer and an outer cover layer.

Preferably, the solid center comprises the HNP's of the present invention. In another embodiment, the inner cover layer comprises the highly-neutralized acid copolymers of the present invention. In an alternative embodiment, the outer core layer comprises the highly-neutralized acid copolymers of the present invention.

At least one of the outer core layers is formed of a resilient rubber-based component comprising a high-Mooney-viscosity rubber, and a crosslinking agent present in an amount from about 20 to about 40 parts per hundred, from about 30 to about 38 parts per hundred, and most preferably about 37 parts per hundred. It should be understood that the term "parts per hundred" is with reference to the rubber by weight.

When the golf ball of the present invention includes an intermediate layer, such as an outer core layer or an inner cover layer, any or all of these layer(s) may comprise thermoplastic and thermosetting material, but preferably the intermediate layer(s), if present, comprise any suitable material, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid which are available under the trademark SURLYN® of E.I. DuPont de Nemours & Co., of Wilmington, Del., or IOTEK® or ESCOR® of Exxon. These are copolymers or terpolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel or the like, in which the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include methacrylic, crotonic, maleic, fumaric or itaconic acid.

This golf ball can likewise include one or more homopolymeric or copolymeric inner cover materials, such as:

- (1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;
- (2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst;
- (3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates, in particular PPDI-based thermoplastic polyurethanes, and those disclosed in U.S. Pat. No. 5,334,673;

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- (4) Polyureas, such as those disclosed in U.S. Pat. No. 5,484,870;
- (5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly(caprolactam), and blends of polyamides with SURLYN®, polyethylene, ethylene copolymers, ethylene-propylene-non-conjugated diene terpolymer, and the like;
- (6) Acrylic resins and blends of these resins with poly vinyl chloride, elastomers, and the like;
- (7) Thermoplastics, such as urethane; olefinic thermoplastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer; block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly(ether-amide), such as PEBAX®, sold by ELF Atochem of Philadelphia, Pa.;
- (8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene as sold under the trademark NORYL® by General Electric Company of Pittsfield, Mass.;
- (9) Thermoplastic polyesters, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified, poly(trimethylene terephthalate), and elastomers sold under the trademarks HYTREL® by E.I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD® by General Electric Company of Pittsfield, Mass.;
- (10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene or ethylene vinyl acetate or other elastomers; and
- (11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

Preferably, the inner cover includes polymers, such as ethylene, propylene, butene-1 or hexane-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. More preferably, in a low spin rate embodiment designed for maximum distance, the acrylic or methacrylic acid is present in about 16 to 35 weight percent, making the ionomer a high modulus ionomer. In a higher spin embodiment, the inner cover layer includes an ionomer where an acid is present in about 10 to 15 weight percent and includes a softening comonomer. Additionally, high-density polyethylene ("HDPE"), low-density polyethylene ("LDPE"), LLDPE, and homo- and co-polymers of polyolefin are suitable for a variety of golf ball layers.

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In one embodiment, the outer cover preferably includes a polyurethane composition comprising the reaction product of at least one polyisocyanate, polyol, and at least one curing agent. Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"); polymeric MDI; carbodiimide-modified liquid MDI; 4,4'-dicyclohexylmethane diisocyanate ("H₁₂MDI"); p-phenylene diisocyanate ("PPDI"); m-phenylene diisocyanate ("MPDI"); toluene diisocyanate ("TDI"); 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"); isophoronediiisocyanate ("IPDI"); hexamethylene diisocyanate ("HDI"); naphthalene diisocyanate ("NDI"); xylene diisocyanate ("XDI"); p-tetramethylxylene diisocyanate ("p-TMXDI"); m-tetramethylxylene diisocyanate ("m-TMXDI"); ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate ("TMDI"); tetracene diisocyanate; naphthalene diisocyanate; anthracene diisocyanate; isocyanurate of toluene diisocyanate; uretdione of hexamethylene diisocyanate; and mixtures thereof. Polyisocyanates are known to those of ordinary skill in the art as having more than one isocyanate group, e.g., di-isocyanate, tri-isocyanate, and tetra-isocyanate. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term "MDI" includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 7.5% NCO, and more preferably, less than about 7.0%.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol. Examples include, but are not limited to, polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

In another embodiment, polyester polyols are included in the polyurethane material of the invention. Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol; polybutylene adipate glycol; polyethylene propylene adipate glycol; o-phthalate-1,6-hexanediol; poly(hexamethylene adipate) glycol; and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

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In another embodiment, polycaprolactone polyols are included in the materials of the invention. Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In yet another embodiment, the polycarbonate polyols are included in the polyurethane material of the invention. Suitable polycarbonates include, but are not limited to, polyphthalate carbonate and poly(hexamethylene carbonate) glycol. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups. In one embodiment, the molecular weight of the polyol is from about 200 to about 4000.

Polyamine curatives are also suitable for use in the polyurethane composition of the invention and have been found to improve cut, shear, and impact resistance of the resultant balls. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline) ("MCDEA"); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyl-diamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine ("MPDA"); 4,4'-methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-methylene-bis-(2,6-diethylaniline) ("MDEA"); 4,4'-methylene-bis-(2,3-dichloroaniline) ("MDCA"); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as ETHACURE 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives, which include both primary and secondary amines, preferably have molecular weights ranging from about 64 to about 2000.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β-hydroxyethyl)ether; hydroquinone-di-(β-hydroxyethyl) ether; and mixtures thereof. Preferred hydroxy-terminated curatives include 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol, and mixtures thereof. Preferably, the hydroxy-terminated curatives have molecular weights ranging from about 48 to 2000. It should be understood that molecular weight, as used herein, is the absolute weight average molecular weight and would be understood as such by one of ordinary skill in the art.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or

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mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

In a preferred embodiment of the present invention, saturated polyurethanes used to form cover layers, preferably the outer cover layer, and may be selected from among both

castable thermoset and thermoplastic polyurethanes. In this embodiment, the saturated polyurethanes of the present invention are substantially free of aromatic groups or moieties. Saturated polyurethanes suitable for use in the invention are a product of a reaction between at least one polyurethane prepolymer and at least one saturated curing agent. The polyurethane prepolymer is a product formed by a reaction between at least one saturated polyol and at least one saturated diisocyanate. As is well known in the art, a catalyst may be employed to promote the reaction between the curing agent and the isocyanate and polyol.

Saturated diisocyanates which can be used include, without limitation, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; dicyclohexylmethane diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isophorone diisocyanate ("IPDI"); methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate ("TMDI"). The most preferred saturated diisocyanates are 4,4'-dicyclohexylmethane diisocyanate ("HMDI") and isophorone diisocyanate ("IPDI").

Saturated polyols which are appropriate for use in this invention include without limitation polyether polyols such as polytetramethylene ether glycol and poly(oxypropylene) glycol. Suitable saturated polyester polyols include polyethylene adipate glycol, polyethylene propylene adipate glycol, polybutylene adipate glycol, polycarbonate polyol and ethylene oxide-capped polyoxypropylene diols. Saturated polycaprolactone polyols which are useful in the invention include diethylene glycol-initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, 1,6-hexanediol-initiated polycaprolactone; trimethylol propane-initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, and polytetramethylene ether glycol-initiated polycaprolactone. The most preferred saturated polyols are polytetramethylene ether glycol and PTMEG-initiated polycaprolactone.

Suitable saturated curatives include 1,4-butanediol, ethylene glycol, diethylene glycol, polytetramethylene ether glycol, propylene glycol; trimethanolpropane; tetra-(2-hydroxypropyl)-ethylenediamine; isomers and mixtures of isomers of cyclohexyldimethylol, isomers and mixtures of isomers of cyclohexane bis(methylamine); triisopropanolamine; ethylene diamine; diethylene triamine; triethylene tetramine; tetraethylene pentamine; 4,4'-dicyclohexylmethane diamine; 2,2,4-trimethyl-1,6-hexanediamine; 2,4,4-trimethyl-1,6-hexanediamine; diethyleneglycol di-(aminopropyl)ether; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,2-bis-(sec-butylamino)cyclohexane; 1,4-bis-(sec-butylamino)cyclohexane; isophorone diamine; hexamethylene diamine; propylene diamine; 1-methyl-2,4-cyclohexyl diamine; 1-methyl-2,6-cyclohexyl diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; imido-bis-propylamine; isomers and mixtures of isomers of diaminocyclohexane; monoethanolamine; diethanolamine; triethanolamine; monoisopropanolamine; and diisopropanolamine. The most preferred saturated curatives are 1,4-butanediol, 1,4-cyclohexyldimethylol and 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

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The compositions of the invention may also be polyurea-based, which are distinctly different from polyurethane compositions, but also result in desirable aerodynamic and aesthetic characteristics when used in golf ball components. The polyurea-based compositions are preferably saturated in nature.

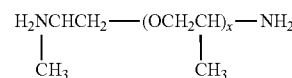
Without being bound to any particular theory, it is now believed that substitution of the long chain polyol segment in the polyurethane prepolymer with a long chain polyamine oligomer soft segment to form a polyurea prepolymer, improves shear, cut, and resiliency, as well as adhesion to other components. Thus, the polyurea compositions of this invention may be formed from the reaction product of an isocyanate and polyamine prepolymer crosslinked with a curing agent. For example, polyurea-based compositions of the invention may be prepared from at least one isocyanate, at least one polyether amine, and at least one diol curing agent or at least one diamine curing agent.

Any polyamine available to one of ordinary skill in the art is suitable for use in the polyurea prepolymer. Polyether amines are particularly suitable for use in the prepolymer. As used herein, "polyether amines" refer to at least polyoxyalkyleneamines containing primary amino groups attached to the terminus of a polyether backbone. Due to the rapid reaction of isocyanate and amine, and the insolubility of many urea products, however, the selection of diamines and polyether amines is limited to those allowing the successful formation of the polyurea prepolymers. In one embodiment, the polyether backbone is based on tetramethylene, propylene, ethylene, trimethylolpropane, glycerin, and mixtures thereof.

Suitable polyether amines include, but are not limited to, methyldiethanolamine; polyoxyalkylenediamines such as, polytetramethylene ether diamines, polyoxypropylenetriamine, and polyoxypropylene diamines; poly(ethylene oxide capped oxypropylene) ether diamines; propylene oxide-based triamines; triethyleneglycoldiamines; trimethylolpropane-based triamines; glycerin-based triamines; and mixtures thereof. In one embodiment, the polyether amine used to form the prepolymer is JEFFAMINE® D2000 (manufactured by Huntsman Chemical Co. of Austin, Tex.).

The molecular weight of the polyether amine for use in the polyurea prepolymer may range from about 100 to about 5000. As used herein, the term "about" is used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range. In one embodiment, the polyether amine molecular weight is about 200 or greater, preferably about 230 or greater. In another embodiment, the molecular weight of the polyether amine is about 4000 or less. In yet another embodiment, the molecular weight of the polyether amine is about 600 or greater. In still another embodiment, the molecular weight of the polyether amine is about 3000 or less. In yet another embodiment, the molecular weight of the polyether amine is between about 1000 and about 3000, and more preferably is between about 1500 to about 2500. Because lower molecular weight polyether amines may be prone to forming solid polyureas, a higher molecular weight oligomer, such as Jeffamine D2000, is preferred.

In one embodiment, the polyether amine has the generic structure:

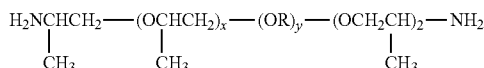


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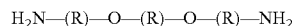
wherein the repeating unit x has a value ranging from about 1 to about 70. Even more preferably, the repeating unit may be from about 5 to about 50, and even more preferably is from about 12 to about 35.

In another embodiment, the polyether amine has the generic structure:



wherein the repeating units x and z have combined values from about 3.6 to about 8 and the repeating unit y has a value ranging from about 9 to about 50, and wherein R is $-(\text{CH}_2)_a-$, where "a" may be a repeating unit ranging from about 1 to about 10.

In yet another embodiment, the polyether amine has the generic structure:



wherein R is $-(\text{CH}_2)_a-$, and "a" may be a repeating unit ranging from about 1 to about 10.

As briefly discussed above, some amines may be unsuitable for reaction with the isocyanate because of the rapid reaction between the two components. In particular, shorter chain amines are fast reacting. In one embodiment, however, a hindered secondary diamine may be suitable for use in the prepolymer. Without being bound to any particular theory, it is believed that an amine with a high level of steric hindrance, e.g., a tertiary butyl group on the nitrogen atom, has a slower reaction rate than an amine with no hindrance or a low level of hindrance. For example, 4,4'-bis-(sec-butylamino)-dicyclohexylmethane (CLEARLINK® 1000) may be suitable for use in combination with an isocyanate to form the polyurea prepolymer.

Any isocyanate available to one of ordinary skill in the art is suitable for use in the polyurea prepolymer. Isocyanates for use with the present invention include aliphatic, cycloaliphatic, araliphatic, aromatic, any derivatives thereof, and combinations of these compounds having two or more isocyanate (NCO) groups per molecule. The isocyanates may be organic polyisocyanate-terminated prepolymers. The isocyanate-containing reactable component may also include any isocyanate-functional monomer, dimer, trimer, or multimeric adduct thereof, prepolymer, quasi-prepolymer, or mixtures thereof. Isocyanate-functional compounds may include monoisocyanates or polyisocyanates that include any isocyanate functionality of two or more.

Suitable isocyanate-containing components include diisocyanates having the generic structure: $\text{O}=\text{C}=\text{N}-\text{R}-\text{N}=\text{C}=\text{O}$, where R is preferably a cyclic, aromatic, or linear or branched hydrocarbon moiety containing from about 1 to about 20 carbon atoms. The diisocyanate may also contain one or more cyclic groups or one or more phenyl groups. When multiple cyclic or aromatic groups are present, linear and/or branched hydrocarbons containing from about 1 to about 10 carbon atoms can be present as spacers between the cyclic or aromatic groups. In some cases, the cyclic or aromatic group(s) may be substituted at the 2-, 3-, and/or 4-positions, or at the ortho-, meta-, and/or para-positions, respectively. Substituted groups may include, but are not limited to, halogens, primary, secondary, or tertiary hydrocarbon groups, or a mixture thereof.

Examples of diisocyanates that can be used with the present invention include, but are not limited to, substituted and isomeric mixtures including 2,2'-, 2,4'-, and 4,4'-diphe-

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nylmethane diisocyanate (MDI); 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI); toluene diisocyanate (TDI); polymeric MDI; carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate; para-phenylene diisocyanate (PPDI); meta-phenylene diisocyanate (MPDI); triphenyl methane-4,4'- and triphenyl methane-4,4'-triisocyanate; naphthylene-1,5-diisocyanate; 2,4'-, 4,4'-, and 2,2-biphenyl diisocyanate; polyphenyl polymethylene polyisocyanate (PMDI); mixtures of MDI and PMDI; mixtures of PMDI and TDI; ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,2-diisocyanate; tetramethylene-1,3-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate (HDI); octamethylene diisocyanate; decamethylene diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl-cyclohexylene diisocyanate (HTDI); 2,4-methylcyclohexane diisocyanate; 2,6-methylcyclohexane diisocyanate; 4,4'-dicyclohexyl diisocyanate; 2,4'-dicyclohexyl diisocyanate; 1,3,5-cyclohexane triisocyanate; isocyanatomethylcyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isocyanatoethylcyclohexane isocyanate; bis(isocyanatomethyl)-cyclohexane diisocyanate; 4,4'-bis(isocyanatomethyl)dicyclohexane; 2,4'-bis(isocyanatomethyl)dicyclohexane; isophorone diisocyanate (IPDI); triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate (TMDI); 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI); 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; 1,2-, 1,3-, and 1,4-phenylene diisocyanate; aromatic aliphatic isocyanate, such as 1,2-, 1,3-, and 1,4-xylylene diisocyanate; meta-tetramethylxylylene diisocyanate (m-TMXDI); para-tetramethylxylylene diisocyanate (p-TMXDI); trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylxylylene diisocyanate, isocyanurate of hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate, and mixtures thereof; dimerized uredione of any polyisocyanate, such as uretdione of toluene diisocyanate, uretdione of hexamethylene diisocyanate, and mixtures thereof; modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof.

Examples of saturated diisocyanates that can be used with the present invention include, but are not limited to, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate (HDI); octamethylene diisocyanate; decamethylene diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl-cyclohexylene diisocyanate (HTDI); 2,4-methylcyclohexane diisocyanate; 2,6-methylcyclohexane diisocyanate; 4,4'-dicyclohexyl diisocyanate; 2,4'-dicyclohexyl diisocyanate; 1,3,5-cyclohexane triisocyanate; isocyanatomethylcyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isocyanatoethylcyclohexane isocyanate; bis(isocyanatomethyl)-cyclohexane diisocyanate; 4,4'-bis(isocyanatomethyl)dicyclohexane; 2,4'-bis(isocyanatomethyl)dicyclohexane; isophorone diisocyanate (IPDI); triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate (TMDI); 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI); 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; and mixtures thereof. Aromatic aliphatic isocyanates may also be

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used to form light stable materials. Examples of such isocyanates include 1,2-, 1,3-, and 1,4-xylene diisocyanate; meta-tetramethylxylene diisocyanate (m-TMXDI); para-tetramethylxylene diisocyanate (p-TMXDI); trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylxylene diisocyanate, isocyanurate of hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate, and mixtures thereof; dimerized uretdione of any polyisocyanate, such as uretdione of toluene diisocyanate, uretdione of hexamethylene diisocyanate, and mixtures thereof; modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof. In addition, the aromatic aliphatic isocyanates may be mixed with any of the saturated isocyanates listed above for the purposes of this invention.

The number of unreacted NCO groups in the polyurea prepolymer of isocyanate and polyether amine may be varied to control such factors as the speed of the reaction, the resultant hardness of the composition, and the like. For instance, the number of unreacted NCO groups in the polyurea prepolymer of isocyanate and polyether amine may be less than about 14 percent. In one embodiment, the polyurea prepolymer has from about 5 percent to about 11 percent unreacted NCO groups, and even more preferably has from about 6 to about 9.5 percent unreacted NCO groups. In one embodiment, the percentage of unreacted NCO groups is about 3 percent to about 9 percent. Alternatively, the percentage of unreacted NCO groups in the polyurea prepolymer may be about 7.5 percent or less, and more preferably, about 7 percent or less. In another embodiment, the unreacted NCO content is from about 2.5 percent to about 7.5 percent, and more preferably from about 4 percent to about 6.5 percent.

When formed, polyurea prepolymers may contain about 10 percent to about 20 percent by weight of the prepolymer of free isocyanate monomer. Thus, in one embodiment, the polyurea prepolymer may be stripped of the free isocyanate monomer. For example, after stripping, the prepolymer may contain about 1 percent or less free isocyanate monomer. In another embodiment, the prepolymer contains about 0.5 percent by weight or less of free isocyanate monomer.

The polyether amine may be blended with additional polyols to formulate copolymers that are reacted with excess isocyanate to form the polyurea prepolymer. In one embodiment, less than about 30 percent polyol by weight of the copolymer is blended with the saturated polyether amine. In another embodiment, less than about 20 percent polyol by weight of the copolymer, preferably less than about 15 percent by weight of the copolymer, is blended with the polyether amine. The polyols listed above with respect to the polyurethane prepolymer, e.g., polyether polyols, polycaprolactone polyols, polyester polyols, polycarbonate polyols, hydrocarbon polyols, other polyols, and mixtures thereof, are also suitable for blending with the polyether amine. The molecular weight of these polymers may be from about 200 to about 4000, but also may be from about 1000 to about 3000, and more preferably are from about 1500 to about 2500.

The polyurea composition can be formed by crosslinking the polyurea prepolymer with a single curing agent or a blend of curing agents. The curing agent of the invention is preferably an amine-terminated curing agent, more preferably a secondary diamine curing agent so that the composition contains only urea linkages. In one embodiment, the amine-terminated curing agent may have a molecular weight of about 64 or greater. In another embodiment, the molecular weight of the amine-curing agent is about 2000 or less. As discussed above, certain amine-terminated curing agents may

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be modified with a compatible amine-terminated freezing point depressing agent or mixture of compatible freezing point depressing agents.

Suitable amine-terminated curing agents include, but are not limited to, ethylene diamine; hexamethylene diamine; 1-methyl-2,6-cyclohexyl diamine; tetrahydroxypropylene ethylene diamine; 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 4,4'-dicyclohexylmethane diamine; 1,4-cyclohexane-bis-(methylamine); 1,3-cyclohexane-bis-(methylamine); diethylene glycol di-(aminopropyl)ether; 2-methylpentamethylene-diamine; diaminocyclohexane; diethylene triamine; triethylene tetramine; tetraethylene pentamine; propylene diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; dipropylene triamine; imido-bis-propylamine; monoethanolamine, diethanolamine; triethanolamine; monoisopropanolamine, diisopropanolamine; isophoronediamine; 4,4'-methylenebis-(2-chloroaniline); 3,5; dimethylthio-2,4-toluenediamine; 3,5-dimethylthio-2,6-toluenediamine; 3,5-diethylthio-2,4-toluenediamine; 3,5; diethylthio-2,6-toluenediamine; 4,4'-bis-(sec-butylamino)-diphenylmethane and derivatives thereof; 1,4-bis-(sec-butylamino)-benzene; 1,2-bis-(sec-butylamino)-benzene; N,N'-dialkylamino-diphenylmethane; N,N,N',N'-tetrakis(2-hydroxypropyl)ethylene diamine; trimethyleneglycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; 4,4'-methylenebis-(3-chloro-2,6-diethylaniline); 4,4'-methylenebis-(2,6-diethylaniline); meta-phenylenediamine; paraphenylenediamine; and mixtures thereof. In one embodiment, the amine-terminated curing agent is 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

Suitable saturated amine-terminated curing agents include, but are not limited to, ethylene diamine; hexamethylene diamine; 1-methyl-2,6-cyclohexyl diamine; tetrahydroxypropylene ethylene diamine; 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 4,4'-dicyclohexylmethane diamine; 4,4'-methylenebis-(2,6-diethylaminocyclohexane); 1,4-cyclohexane-bis-(methylamine); 1,3-cyclohexane-bis-(methylamine); diethylene glycol di-(aminopropyl)ether; 2-methylpentamethylene-diamine; diaminocyclohexane; diethylene triamine; triethylene tetramine; tetraethylene pentamine; propylene diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; imido-bis-propylamine; monoethanolamine, diethanolamine; triethanolamine; monoisopropanolamine, diisopropanolamine; isophoronediamine; triisopropanolamine; and mixtures thereof. In addition, any of the polyether amines listed above may be used as curing agents to react with the polyurea prepolymers.

Suitable catalysts include, but are not limited to bismuth catalyst, oleic acid, triethylenediamine (DABCO®-33LV), di-butyltin dilaurate (DABCO®-T12) and acetic acid. The most preferred catalyst is di-butyltin dilaurate (DABCO®-T12). DABCO® materials are manufactured by Air Products and Chemicals, Inc.

Thermoplastic materials may be blended with other thermoplastic materials, but thermosetting materials are difficult if not impossible to blend homogeneously after the thermosetting materials are formed. Preferably, the saturated polyurethane comprises from about 1% to about 100%, more preferably from about 10% to about 75% of the cover com-

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position and/or the intermediate layer composition. About 90% to about 10%, more preferably from about 90% to about 25% of the cover and/or the intermediate layer composition is comprised of one or more other polymers and/or other materials as described below. Such polymers include, but are not limited to polyurethane/polyurea ionomers, polyurethanes or polyureas, epoxy resins, polyethylenes, polyamides and polyesters, polycarbonates and polyacrylin. Unless otherwise stated herein, all percentages are given in percent by weight of the total composition of the golf ball layer in question.

Polyurethane prepolymers are produced by combining at least one polyol, such as a polyether, polycaprolactone, polycarbonate or a polyester, and at least one isocyanate. Thermosetting polyurethanes are obtained by curing at least one polyurethane prepolymer with a curing agent selected from a polyamine, triol or tetraol. Thermoplastic polyurethanes are obtained by curing at least one polyurethane prepolymer with a diol curing agent. The choice of the curatives is critical because some urethane elastomers that are cured with a diol and/or blends of diols do not produce urethane elastomers with the impact resistance required in a golf ball cover. Blending the polyamine curatives with diol cured urethane elastomeric formulations leads to the production of thermoset urethanes with improved impact and cut resistance.

Thermoplastic polyurethanes may be blended with suitable materials to produce a thermoplastic end product. Examples of such additional materials may include ionomers such as the SURLYN®, ESCOR® and IOTEK® copolymers described above.

Other suitable materials which may be combined with the saturated polyurethanes in forming the cover and/or intermediate layer(s) of the golf balls of the invention include ionic or non-ionic polyurethanes and polyureas, epoxy resins, polyethylenes, polyamides and polyesters. For example, the cover and/or intermediate layer may be formed from a blend of at least one saturated polyurethane and thermoplastic or thermoset ionic and non-ionic urethanes and polyurethanes, cationic urethane ionomers and urethane epoxies, ionic and non-ionic polyureas and blends thereof. Examples of suitable urethane ionomers are disclosed in U.S. Pat. No. 5,692,974 entitled "Golf Ball Covers", the disclosure of which is hereby incorporated by reference in its entirety. Other examples of suitable polyurethanes are described in U.S. Pat. No. 5,334,673. Examples of appropriate polyureas are discussed in U.S. Pat. No. 5,484,870 and examples of suitable polyurethanes cured with epoxy group containing curing agents are disclosed in U.S. Pat. No. 5,908,358, the disclosures of which are hereby incorporated herein by reference in their entirety.

A variety of conventional components can be added to the cover compositions of the present invention. These include, but are not limited to, white pigment such as TiO₂, ZnO, optical brighteners, surfactants, processing aids, foaming agents, density-controlling fillers, UV stabilizers and light stabilizers. Saturated polyurethanes are resistant to discoloration. However, they are not immune to deterioration in their mechanical properties upon weathering. Addition of UV absorbers and light stabilizers therefore helps to maintain the tensile strength and elongation of the saturated polyurethane elastomers. Suitable UV absorbers and light stabilizers include TINUVIN® 328, TINUVIN® 213, TINUVIN® 765, TINUVIN® 770 and TINUVIN® 622. The preferred UV absorber is TINUVIN® 328, and the preferred light stabilizer is TINUVIN® 765. TINUVIN® products are available from Ciba-Geigy. Dyes, as well as optical brighteners and fluorescent pigments may also be included in the golf ball covers produced with polymers formed according to the present

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invention. Such additional ingredients may be added in any amounts that will achieve their desired purpose.

Any method known to one of ordinary skill in the art may be used to polyurethanes of the present invention. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogenous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition. Other methods suitable for forming the layers of the present invention include reaction injection molding ("RIM"), liquid injection molding ("LIM"), and pre-reacting the components to form an injection moldable thermoplastic polyurethane and then injection molding, all of which are known to one of ordinary skill in the art.

Additional components which can be added to the polyurethane composition include UV stabilizers and other dyes, as well as optical brighteners and fluorescent pigments and dyes. Such additional ingredients may be added in any amounts that will achieve their desired purpose. It has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the urethane elastomer material can be applied over the core using a variety of application techniques such as spraying, dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Pat. No. 5,733,428, the disclosure of which is hereby incorporated by reference in its entirety.

The outer cover is preferably formed around the inner cover by mixing and introducing the material in the mold halves. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing cores into the mold halves is determined to be approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using centering pins moving into holes in each mold. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity. After the reacting materials have resided in top mold halves for about 40 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture.

A ball cup holds the ball core through reduced pressure (or partial vacuum). Upon location of the coated core in the halves of the mold after gelling for about 40 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit, inverted and mated with other mold halves which, at an appropriate time

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earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

Similarly, U.S. Pat. No. 5,006,297 to Brown et al. and U.S. Pat. No. 5,334,673 to Wu both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. Further, U.S. Pat. Nos. 6,180,040 and 6,180,722 disclose methods of preparing dual core golf balls. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

Depending on the desired properties, balls prepared according to the invention can exhibit substantially the same or higher resilience, or coefficient of restitution ("COR"), with a decrease in compression or modulus, compared to balls of conventional construction. Additionally, balls prepared according to the invention can also exhibit substantially higher resilience, or COR, without an increase in compression, compared to balls of conventional construction. Another measure of this resilience is the "loss tangent," or $\tan \delta$, which is obtained when measuring the dynamic stiffness of an object. Loss tangent and terminology relating to such dynamic properties is typically described according to ASTM D4092-90. Thus, a lower loss tangent indicates a higher resiliency, thereby indicating a higher rebound capacity. Low loss tangent indicates that most of the energy imparted to a golf ball from the club is converted to dynamic energy, i.e., launch velocity and resulting longer distance. The rigidity or compressive stiffness of a golf ball may be measured, for example, by the dynamic stiffness. A higher dynamic stiffness indicates a higher compressive stiffness. To produce golf balls having a desirable compressive stiffness, the dynamic stiffness of the crosslinked reaction product material should be less than about 50,000 N/m at -50°C . Preferably, the dynamic stiffness should be between about 10,000 and 40,000 N/m at -50°C ., more preferably, the dynamic stiffness should be between about 20,000 and 30,000 N/m at -50°C .

The molding process and composition of golf ball portions typically results in a gradient of material properties. Methods employed in the prior art generally exploit hardness to quantify these gradients. Hardness is a qualitative measure of static modulus and does not represent the modulus of the material at the deformation rates associated with golf ball use, i.e., impact by a club. As is well known to one skilled in the art of polymer science, the time-temperature superposition principle may be used to emulate alternative deformation rates. For golf ball portions including polybutadiene, a 1-Hz oscillation at temperatures between 0°C . and -50°C . are believed to be qualitatively equivalent to golf ball impact rates. Therefore, measurement of loss tangent and dynamic stiffness at 0°C . to -50°C . may be used to accurately anticipate golf ball performance, preferably at temperatures between about -20°C . and -50°C .

In another embodiment of the present invention, a golf ball of the present invention is substantially spherical and has a cover with a plurality of dimples formed on the outer surface thereof.

U.S. application Ser. No. 10/230,015, now U.S. Publication No. 2003/0114565, and U.S. application Ser. No. 10/108,793, now U.S. Publication No. 2003/0050373, which are incorporated by reference herein in their entirety, discuss soft, high resilient ionomers, which are preferably from neutralizing the acid copolymer(s) of at least one E/X/Y copolymer, where E is ethylene, X is the α,β -ethylenically unsaturated carboxylic acid, and Y is a softening co-monomer. X is preferably present in 2-30 (preferably 4-20, most preferably 5-15)

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wt. % of the polymer, and Y is preferably present in 17-40 (preferably 20-40, and more preferably 24-35) wt. % of the polymer. Preferably, the melt index (MI) of the base resin is at least 20, or at least 40, more preferably, at least 75 and most preferably at least 150. Particular soft, resilient ionomers included in this invention are partially neutralized ethylene/(meth) acrylic acid/butyl(meth)acrylate copolymers having an MI and level of neutralization that results in a melt processable polymer that has useful physical properties. The copolymers are at least partially neutralized. Preferably at least 40, or, more preferably at least 55, even more preferably about 70, and most preferably about 80 of the acid moiety of the acid copolymer is neutralized by one or more alkali metal, transition metal, or alkaline earth metal cations. Cations useful in making the ionomers of this invention comprise lithium, sodium, potassium, magnesium, calcium, barium, or zinc, or a combination of such cations.

The invention also relates to a "modified" soft, resilient thermoplastic ionomer that comprises a melt blend of (a) the acid copolymers or the melt processable ionomers made therefrom as described above and (b) one or more organic acid(s) or salt(s) thereof, wherein greater than 80%, preferably greater than 90% of all the acid of (a) and of (b) is neutralized. Preferably, 100% of all the acid of (a) and (b) is neutralized by a cation source. Preferably, an amount of cation source in excess of the amount required to neutralize 100% of the acid in (a) and (b) is used to neutralize the acid in (a) and (b). Blends with fatty acids or fatty acid salts are preferred.

The organic acids or salts thereof are added in an amount sufficient to enhance the resilience of the copolymer. Preferably, the organic acids or salts thereof are added in an amount sufficient to substantially remove remaining ethylene crystallinity of the copolymer.

Preferably, the organic acids or salts are added in an amount of at least about 5% (weight basis) of the total amount of copolymer and organic acid(s). More preferably, the organic acids or salts thereof are added in an amount of at least about 15%, even more preferably at least about 20%. Preferably, the organic acid(s) are added in an amount up to about 50% (weight basis) based on the total amount of copolymer and organic acid. More preferably, the organic acids or salts thereof are added in an amount of up to about 40%, more preferably, up to about 35%. The non-volatile, non-migratory organic acids preferably are one or more aliphatic, mono-functional organic acids or salts thereof as described below, particularly one or more aliphatic, mono-functional, saturated or unsaturated organic acids having less than 36 carbon atoms or salts of the organic acids, preferably stearic acid or oleic acid. Fatty acids or fatty acid salts are most preferred.

Processes for fatty acid (salt) modifications are known in the art. Particularly, the modified highly-neutralized soft, resilient acid copolymer ionomers of this invention can be produced by:

(a) melt-blending (1) ethylene, α,β -ethylenically unsaturated C_{3-8} carboxylic acid copolymer(s) or melt-processable ionomer(s) thereof that have their crystallinity disrupted by addition of a softening monomer or other means with (2) sufficient non-volatile, non-migratory organic acids to substantially enhance the resilience and to disrupt (preferably remove) the remaining ethylene crystallinity, and then concurrently or subsequently

(b) adding a sufficient amount of a cation source to increase the level of neutralization of all the acid moieties (including those in the acid copolymer and in the organic acid if the non-volatile, non-migratory organic acid is an organic acid) to the desired level.

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The weight ratio of X to Y in the composition is at least about 1:20. Preferably, the weight ratio of X to Y is at least about 1:15, more preferably, at least about 1:10. Furthermore, the weight ratio of X to Y is up to about 1:1.67, more preferably up to about 1:2. Most preferably, the weight ratio of X to Y in the composition is up to about 1:2.2.

The acid copolymers used in the present invention to make the ionomers are preferably 'direct' acid copolymers (containing high levels of softening monomers). As noted above, the copolymers are at least partially neutralized, preferably at least about 40% of X in the composition is neutralized. More preferably, at least about 55% of X is neutralized. Even more preferably, at least about 70, and most preferably, at least about 80% of X is neutralized. In the event that the copolymer is highly neutralized (e.g., to at least 45%, preferably 50%, 55%, 70%, or 80%, of acid moiety), the MI of the acid copolymer should be sufficiently high so that the resulting neutralized resin has a measurable MI in accord with ASTM D-1238, condition E, at 190° C., using a 2160 gram weight. Preferably this resulting MI will be at least 0.1, preferably at least 0.5, and more preferably 1.0 or greater. Preferably, for highly neutralized acid copolymer, the MI of the acid copolymer base resin is at least 20, or at least 40, at least 75, and more preferably at least 150.

The acid copolymers preferably comprise alpha olefin, particularly ethylene, C₃₋₈ α,β -ethylenically unsaturated carboxylic acid, particularly acrylic and methacrylic acid, and softening monomers, selected from alkyl acrylate, and alkyl methacrylate, wherein the alkyl groups have from 1-8 carbon atoms, copolymers. By "softening," it is meant that the crystallinity is disrupted (the polymer is made less crystalline). While the alpha olefin can be a C₂-C₄ alpha olefin, ethylene is most preferred for use in the present invention. Accordingly, it is described and illustrated herein in terms of ethylene as the alpha olefin.

The acid copolymers, when the alpha olefin is ethylene, can be described as E/X/Y copolymers where E is ethylene, X is the α,β -ethylenically unsaturated carboxylic acid, and Y is a softening comonomer; X is preferably present in 2-30 (preferably 4-20, most preferably 5-15) wt. % of the polymer, and Y is preferably present in 17-40 (preferably 20-40, most preferably 24-35) wt. % of the polymer.

The ethylene-acid copolymers with high levels of acid (X) are difficult to prepare in continuous polymerizers because of monomer-polymer phase separation. This difficulty can be avoided however by use of "co-solvent technology" as described in U.S. Pat. No. 5,028,674, or by employing somewhat higher pressures than those which copolymers with lower acid can be prepared.

Specific acid-copolymers include ethylene/(meth) acrylic acid/n-butyl(meth)acrylate, ethylene/(meth) acrylic acid/iso-butyl(meth)acrylate, ethylene/(meth) acrylic acid/methyl(meth)acrylate, and ethylene/(meth) acrylic acid/ethyl(meth)acrylate terpolymers.

The organic acids employed are aliphatic, mono-functional (saturated, unsaturated, or multi-unsaturated) organic acids, particularly those having fewer than 36 carbon atoms. Also salts of these organic acids may be employed. Fatty acids or fatty acid salts are preferred. The salts may be any of a wide variety, particularly including the barium, lithium, sodium, zinc, bismuth, potassium, strontium, magnesium or calcium salts of the organic acids. Particular organic acids useful in the present invention include caproic acid, caprylic acid, capric acid, lauric acid, stearic acid, behenic acid, erucic acid, oleic acid, and linoleic acid.

The optional filler component is chosen to impart additional density to blends of the previously described compo-

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nents, the selection being dependent upon the different parts (e.g., cover, mantle, core, center, intermediate layers in a multilayered core or ball) and the type of golf ball desired (e.g., one-piece, two-piece, three-piece or multiple-piece ball), as will be more fully detailed below.

Generally, the filler will be inorganic having a density greater than about 4 g/cm³, preferably greater than 5 g/cm³, and will be present in amounts between 0 to about 60 wt. % based on the total weight of the composition. Examples of useful fillers include zinc oxide, barium sulfate, lead silicate and tungsten carbide, as well as the other well-known fillers used in golf balls. It is preferred that the filler materials be non-reactive or almost non-reactive and not stiffen or raise the compression nor reduce the coefficient of restitution significantly.

Additional optional additives useful in the practice of the subject invention include acid copolymer wax (e.g., Allied wax AC 143 believed to be an ethylene/16-18% acrylic acid copolymer with a number average molecular weight of 2,040), which assist in preventing reaction between the filler materials (e.g., ZnO) and the acid moiety in the ethylene copolymer. Other optional additives include TiO₂, which is used as a whitening agent; optical brighteners; surfactants; processing aids; etc.

Ionomers may be blended with conventional ionomeric copolymers (di-, ter-, etc.), using well-known techniques, to manipulate product properties as desired. The blends would still exhibit lower hardness and higher resilience when compared with blends based on conventional ionomers.

Also, ionomers can be blended with non-ionic thermoplastic resins to manipulate product properties. The non-ionic thermoplastic resins would, by way of non-limiting illustrative examples, include thermoplastic elastomers, such as polyurethane, poly-ether-ester, poly-amide-ether, polyether-urea, PEBAX® (a family of block copolymers based on poly-ether-block-amide, commercially supplied by Atochem), styrene-butadiene-styrene (SBS) block copolymers, styrene (ethylene-butylene)-styrene block copolymers, etc., poly amide (oligomeric and polymeric), polyesters, polyolefins including PE, PP, E/P copolymers, etc., ethylene copolymers with various comonomers, such as vinyl acetate, (meth)acrylates, (meth)acrylic acid, epoxy-functionalized monomer, CO, etc., functionalized polymers with maleic anhydride grafting, epoxidization etc., elastomers, such as EPDM, metallocene catalyzed PE and copolymer, ground up powders of the thermoset elastomers, etc. Such thermoplastic blends comprise about 1% to about 99% by weight of a first thermoplastic and about 99% to about 1% by weight of a second thermoplastic.

Additionally, the compositions of U.S. Pat. Nos. 6,953,820 and 6,653,382, both of which are incorporated herein in their entirety, discuss compositions having high COR when formed into solid spheres.

The thermoplastic composition of this invention comprises a polymer which, when formed into a sphere that is 1.50 to 1.54 inches in diameter, has a coefficient of restitution when measured by firing the sphere at an initial velocity of 125 ft/s against a steel plate positioned 3 ft from the point where initial velocity and rebound velocity are determined and by dividing the rebound velocity from the plate by the initial velocity and an Atti compression of no more than 100.

Initial velocity of a golf ball after impact with a golf club is governed by the United States Golf Association ("USGA"). The USGA requires that a regulation golf ball can have an initial velocity of no more than 250 ft/s \pm 2% (effectively 255 ft/s). The USGA initial velocity limit is related to the ultimate distance that a golf ball may travel (280 yards \pm 6%), and is

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also related to the COR. The COR is the ratio of the a) relative velocity between two objects after direct impact to the b) relative velocity before impact. As a result, the COR can vary from 0 to 1.0, with 1.0 being equivalent to a perfectly or completely elastic collision and 0 being equivalent to a perfectly plastic or completely inelastic collision.

One conventional technique for measuring COR uses a golf ball or sphere, an air cannon, and a stationary steel plate. The steel plate provides an impact surface weighing about 100 lb (45 kg). A pair of ballistic light screens, which measure ball velocity, are spaced apart and located between the air cannon and the steel plate. The golf ball is fired from the air cannon toward the steel plate over a range of test velocities from 50 ft/s to 180 ft/s. As the ball travels toward the steel plate, it activates each light screen so that the time at each light screen is measured. This provides an incoming time period proportional to the ball incoming velocity. The ball impacts the steel plate and rebounds through the light screens, which again measure the time period required to transit between the light screens. This provides an outgoing transit time period proportional to the ball outgoing velocity. The COR can be calculated by the ratio of the outgoing transit time period to the incoming transit time period, $COR = T_{out}/T_{in}$.

Another COR measuring method uses a titanium disk. The titanium disk, intending to simulate a golf club, is circular and has a diameter of about 4 inches and has a mass of about 200 g. The impact face of the titanium disk may also be flexible and has its own COR, as discussed further below. The disk is mounted on an X-Y-Z table so that its position can be adjusted relative to the launching device prior to testing. A pair of ballistic light screens are spaced apart and located between the launching device and the titanium disk. The ball is fired from the launching device toward the titanium disk at a predetermined test velocity. As the ball travels toward the titanium disk, it activates each light screen so that the time period to transit between the light screens is measured. This provides an incoming transit time period proportional to the ball incoming velocity. The ball impacts the titanium disk, and rebounds through the light screens which measure the time period to transit between the light screens. This provides an outgoing transit time period proportional to the ball's outgoing velocity. Coefficient of restitution can be calculated from the ratio of the outgoing time period to the incoming time period along with the mass of the disk and ball: $COR = [(T_{out}/T_{in})(M_e + M_b) + M_b]/M_e$.

The thermoplastic composition of this invention preferably comprises (a) aliphatic, mono-functional organic acid(s) having fewer than 36 carbon atoms; and (b) ethylene, C_3 to C_8 α,β -ethylenically unsaturated carboxylic acid copolymer(s) and ionomer(s) thereof, wherein greater than 90%, preferably near 100%, and more preferably 100% of all the acid of (a) and (b) are neutralized.

The thermoplastic composition preferably comprises melt-processable, highly-neutralized (greater than 90%, preferably near 100%, and more preferably 100%) polymer of (1) ethylene, C_3 to C_8 α,β -ethylenically unsaturated carboxylic acid copolymers that have their crystallinity disrupted by addition of a softening monomer or other means such as high acid levels, and (2) non-volatile, non-migratory agents such as organic acids (or salts) selected for their ability to substantially or totally suppress any remaining ethylene crystallinity. Agents other than organic acids (or salts) may be used.

It has been found that, by modifying an acid copolymer or ionomer with a sufficient amount of specific organic acids (or salts thereof); it is possible to highly neutralize the acid copolymer without losing processability or properties such as elongation and toughness. The organic acids employed in the

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present invention are aliphatic, mono-functional, saturated or unsaturated organic acids, particularly those having fewer than 36 carbon atoms, and particularly those that are non-volatile and non-migratory and exhibit ionic array plasticizing and ethylene crystallinity suppression properties.

With the addition of sufficient organic acid, greater than 90%, nearly 100%, and preferably 100% of the acid moieties in the acid copolymer from which the ionomer is made can be neutralized without losing the processability and properties of elongation and toughness.

The melt-processable, highly-neutralized acid copolymer ionomer can be produced by the following:

(a) melt-blending (1) ethylene α,β -ethylenically unsaturated C_{3-8} carboxylic acid copolymer(s) or melt-processable ionomer(s) thereof (ionomers that are not neutralized to the level that they have become intractable, that is not melt-processable) with (1) one or more aliphatic, mono-functional, saturated or unsaturated organic acids having fewer than 36 carbon atoms or salts of the organic acids, and then concurrently or subsequently

(b) adding a sufficient amount of a cation source to increase the level of neutralization all the acid moieties (including those in the acid copolymer and in the organic acid) to greater than 90%, preferably near 100%, more preferably to 100%.

Preferably, highly-neutralized thermoplastics of the invention can be made by:

(a) melt-blending (1) ethylene, α,β -ethylenically unsaturated C_{3-8} carboxylic acid copolymer(s) or melt-processable ionomer(s) thereof that have their crystallinity disrupted by addition of a softening monomer or other means with (2) sufficient non-volatile, non-migratory agents to substantially remove the remaining ethylene crystallinity, and then concurrently or subsequently

(b) adding a sufficient amount of a cation source to increase the level of neutralization all the acid moieties (including those in the acid copolymer and in the organic acid if the non-volatile, non-migratory agent is an organic acid) to greater than 90%, preferably near 100%, more preferably to 100%.

The acid copolymers used in the present invention to make the ionomers are preferably 'direct' acid copolymers. They are preferably alpha olefin, particularly ethylene, C_{3-8} α,β -ethylenically unsaturated carboxylic acid, particularly acrylic and methacrylic acid, copolymers. They may optionally contain a third softening monomer. By "softening," it is meant that the crystallinity is disrupted (the polymer is made less crystalline). Suitable "softening" comonomers are monomers selected from alkyl acrylate, and alkyl methacrylate, wherein the alkyl groups have from 1-8 carbon atoms.

The acid copolymers, when the alpha olefin is ethylene, can be described as E/X/Y copolymers where E is ethylene, X is the α,β -ethylenically unsaturated carboxylic acid, and Y is a softening comonomer. X is preferably present in 3-30 (preferably 4-25, most preferably 5-20) wt. % of the polymer, and Y is preferably present in 0-30 (alternatively 3-25 or 10-23) wt. % of the polymer.

In one embodiment, golf balls made with the cores of the invention enjoy high COR at relatively low club speeds. The COR of these balls is higher than the COR of similar balls with higher compression cores at relatively low club speeds. At higher club speeds, however, the COR of golf balls with low compression cores can be lower than the COR of balls with higher compression cores. As illustrated herein, a first golf ball with a 1.505-inch diameter core and a core compression of 48 (hereinafter "Sample-48") and a second golf ball with a 1.515-inch diameter core and a core compression of 80 (hereinafter "Sample-80") were subject to the following dis-

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tance and COR tests. Sample-48 and Sample-80 have essentially the same size core and similar dual-layer cover. The single most significant difference between these two balls is the compression of the respective cores.

As used in the ball speed test, the “average driver set-up” refers to a set of launch conditions, i.e., at a club head speed to which a mechanical golf club has been adjusted so as to generate a ball speed of about 140 ft/s. Similarly, the “standard driver set-up” refers to a similar ball speed at launch conditions of about 160 ft/s; the “Pro 167 set-up” refers to a ball speed at launch conditions of about 167 ft/s; and the “Big Pro 175 set-up” refers to a ball speed at launch conditions of about 175 ft/s. Also, as used in the COR test, the mass plate is a 45-kg plate (100 lb) against which the balls strike at the indicated speed. The 200-g solid plate is a smaller mass that the balls strike and resembles the mass of a club head. The 199.8-g calibration plate resembles a driver with a flexible face that has a COR of 0.830.

The ball speed test results show that while Sample-48 holds a ball speed advantage at club speeds of 140 ft/s to 160 ft/s launch conditions, Sample-80 decidedly has better ball speed at 167 ft/s and 175 ft/s launch conditions.

Similarly, the COR test results show that at the higher collision speed (160 ft/s), the COR generally goes down for both balls, but the 199.8-g calibration test shows that the COR of the higher compression Sample-80 is significantly better than the lower compression Sample-48 at the collision speed (160 ft/s). Additionally, while the COR generally goes down for both balls, the rate of decrease is much less for Sample-80 than for Sample-48. Unless specifically noted, COR values used hereafter are measured by either the mass plate method or the 200-gram solid plate method, i.e., where the impact plate is not flexible. Unless otherwise noted, COR values used hereafter are measured by either the mass plate method or the 200-g solid plate method.

Without being limited to any particular theory, the inventors of the present invention believe that at high impact, the ball with lower core compression deforms more than the ball with higher core compression. Such deformation negatively affects the initial velocity and COR of the ball.

In accordance to the present invention, a golf ball is provided with a low compression and high COR layer, which is supported or otherwise reinforced by a low deformation layer.

On the other hand, the low deformation layer in accordance to the present invention may comprise a durable, low deformation material such as metal, rigid plastics, or polymers re-enforced with high strength organic or inorganic fillers or fibers, or blends or composites thereof, as discussed below. Suitable plastics or polymers include, but not limited to, high cis- or trans-polybutadiene, one or more of partially or fully neutralized ionomers including those neutralized by a metal ion source wherein the metal ion is the salt of an organic acid, polyolefins including polyethylene, polypropylene, polybutylene and copolymers thereof including polyethylene acrylic acid or methacrylic acid copolymers, or a terpolymer of ethylene, a softening acrylate class ester such as methyl acrylate, n-butyl-acrylate or iso-butyl-acrylate, and a carboxylic acid such as acrylic acid or methacrylic acid (e.g., terpolymers including polyethylene-methacrylic acid-n or iso-butyl acrylate and polyethylene-acrylic acid-methyl acrylate, polyethylene ethyl or methyl acrylate, polyethylene vinyl acetate, polyethylene glycidyl alkyl acrylates). Suitable polymers also include metallocene catalyzed polyolefins, polyesters, polyamides, non-ionomeric thermoplastic elastomers, copolyether-esters, copolyether-amides, EPR, EPDM, thermoplastic or thermosetting polyurethanes, polyureas, polyurethane ionomers, epoxies, polycarbonates, polybutadiene,

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polyisoprene, and blends thereof. In the case of metallocenes, the polymer may be cross-linked with a free radical source, such as peroxide, or by high radiation.

Spheres were prepared using fully neutralized ionomers A and B.

TABLE I

Sample	Resin Type (%)	Acid Type (%)	Cation (% neut*)	M.I. (g/10 min)
1A	A(60)	Oleic (40)	Mg (100)	1.0
2B	A(60)	Oleic (40)	Mg (105)*	0.9
3C	B(60)	Oleic (40)	Mg (100)	0.9
4D	B(60)	Oleic (40)	Mg (105)*	0.9
5E	B(60)	Stearic (40)	Mg (100)	0.85

A - 76.9% ethylene, 14.8% normal butyl acrylate, 8.3% acrylic acid

B - 75% ethylene, 14.9% normal butyl acrylate, 10.1% acrylic acid

*indicates that cation was sufficient to neutralize 105% of all the acid in the resin and the organic acid.

These compositions were molded into 1.53-inch spheres for which data is presented in the following table.

TABLE II

Sample	Atti Compression	COR @ 125 ft/s
1A	75	0.826
2B	75	0.826
3C	78	0.837
4D	76	0.837
5E	97	0.807

Further testing of commercially available highly neutralized polymers HNP1 and HNP2 had the following properties.

TABLE III

Material Properties		
	HNP1	HNP2
Specific Gravity (g/cm ³)	0.966	0.974
Melt Flow, 190° C., 10-kg load	0.65	1.0
Shore D Flex Bar (40 hr)	47.0	46.0
Shore D Flex Bar (2 week)	51.0	48.0
Flex Modulus, psi (40 hr)	25,800	16,100
Flex Modulus, psi (2 week)	39,900	21,000
DSC Melting Point (° C.)	61.0	61/101
Moisture (ppm)	1500	4500
Weight % Mg	2.65	2.96

TABLE IV

Solid Sphere Data					
	Material				
	HNP1	HNP2	HNP2a	HNP1a	HNP1a/HNP2a (50:50 blend)
Spec. Grav. (g/cm ³)	0.954	0.959	1.153	1.146	1.148
Filler	None	None	Tungsten	Tungsten	Tungsten
Compression	107	83	86	62	72
COR	0.827	0.853	0.844	0.806	0.822
Shore D	51	47	49	42	45
Shore C			79	72	75

These materials are exemplary examples of the preferred center and/or core layer compositions of the present invention. They may also be used as a cover layer herein.

The golf ball components of the present invention, in particular the core (center and/or outer core layers) may be

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formed from a co-polymer of ethylene and an α,β -unsaturated carboxylic acid. In another embodiment, they may be formed from a terpolymer of ethylene, an α,β -unsaturated carboxylic acid, and an n-alkyl acrylate. Preferably, the α,β -unsaturated carboxylic acid is acrylic acid or methacrylic acid. In a preferred embodiment, the n-alkyl acrylate is n-butyl acrylate. Further, in a preferred form, the co- or ter-polymer comprises a level of fatty acid salt greater than 5 phr of the base resin. The preferred fatty acid salt is magnesium oleate or magnesium stearate.

It is highly preferred that the carboxylic acid in the intermediate layer is 100% neutralized with metal ions. The metal ions used to neutralize the carboxylic acid may be any metal ion known in the art. Preferably, the metal ions comprise magnesium ions. If the material used in the intermediate layer is not 100% neutralized, the resultant resilience properties such as COR and initial velocity may not be sufficient to produce the improved initial velocity and distance properties of the present invention.

The golf ball components can comprise various levels of the three components of the co- or terpolymer as follows: from about 60 to about 90% ethylene, from about 8 to about 20% by weight of the α,β -unsaturated carboxylic acid, and from 0% to about 25% of the n-alkyl acrylate. The co- or terpolymer may also contain an amount of a fatty acid salt. The fatty acid salt preferably comprises magnesium oleate. These materials are commercially available from DuPont, under the tradename DuPont HPF®.

In one embodiment, the core and/or core layers (or other intermediate layers) comprises a copolymer of about 81% by weight ethylene and about 19% by weight acrylic acid, wherein 100% of the carboxylic acid groups are neutralized with magnesium ions. The copolymer also contains at least 5 phr of magnesium oleate. Material suitable for use as this layer is available from DuPont under the tradename DuPont HPF SEP 1313-4®.

In a second preferred embodiment, the core and/or core layers (or other intermediate layers) comprise a copolymer of about 85% by weight ethylene and about 15% by weight acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. The copolymer also contains at least 5 phr of magnesium oleate. Material suitable for use as this layer is available from DuPont under the tradename DuPont HPF SEP 1313-3®.

In a third preferred embodiment, the core and/or core layers (or other intermediate layers) comprise a copolymer of about 88% by weight ethylene and about 12% by weight acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. The copolymer also contains at least 5 phr of magnesium oleate. Material suitable for use as this layer is available from DuPont under the tradename DuPont HPF AD1027®.

In a further preferred embodiment, the core and/or core layers (or other intermediate layers) are adjusted to a target specific gravity to enable the ball to be balanced. For a 1.68-inch diameter golf ball having a ball weight of about 1.61 oz, the target specific gravity is about 1.125. It will be appreciated by one of ordinary skill in the art that the target specific gravity will vary based upon the size and weight of the golf ball. The specific gravity is adjusted to the desired target through the use of inorganic fillers. Preferred fillers used for compounding the inner layer to the desired specific gravity include, but are not limited to, tungsten, zinc oxide, barium sulfate and titanium dioxide. Other suitable fillers, in particular nano or hybrid materials, include those described in U.S.

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Pat. No. 6,793,592 and U.S. application Ser. No. 10/037,987, which are incorporated herein, in their entirety, by reference thereto.

Some preferred golf ball layers formed from the above compositions were molded onto a golf ball center using DuPont HPF RX-85®, Dupont HPF SEP 1313-3®, or DuPont HPF SEP 1313-4®. 1) DuPont HPF RX-85®, a copolymer of about 88% ethylene and about 12% acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the copolymer contains a fixed amount of magnesium oleate. This material was compounded to a specific gravity of about 1.125 using tungsten. The Shore D hardness of this material (as measured on the curved surface of the inner cover layer) was about 58 to about 60. 2) DuPont HPF SEP 1313-3®, a copolymer of about 85% ethylene and about 15% acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the copolymer contains a fixed amount of magnesium oleate. This material was compounded to a specific gravity of about 1.125 using tungsten. The Shore D hardness of this material (as measured on the curved surface of the inner cover layer) was about 58-60. 3) DuPont HPF SEP 1313-4®, a copolymer of about 81% ethylene and about 19% acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the copolymer contains a fixed amount of magnesium oleate. This material was compounded to a specific gravity of about 1.125 using tungsten. The Shore D hardness of this material (as measured on the curved surface of the inner cover layer) was about 58-60.

The centers/cores/layers can also comprise various levels of the three components of the terpolymer as follows: from about 60% to 80% ethylene; from about 8% to 20% by weight of the α,β -unsaturated carboxylic acid; and from about 0% to 25% of the n-alkyl acrylate, preferably 5% to 25%. The terpolymer will also contain an amount of a fatty acid salt, preferably magnesium oleate. These materials are commercially available under the trade name DuPont® HPF™. In a preferred embodiment, a terpolymer suitable for the invention will comprise from about 75% to 80% by weight ethylene, from about 8% to 12% by weight of acrylic acid, and from about 8% to 17% by weight of n-butyl acrylate, wherein all of the carboxylic acid is neutralized with magnesium ions, and comprises at least 5 phr of magnesium oleate.

In another preferred embodiment, the cover layer will comprise a terpolymer of about 70% to 75% by weight ethylene, about 10.5% by weight acrylic acid, and about 15.5% to 16.5% by weight n-butyl acrylate. The acrylic acid groups are 100% neutralized with magnesium ions. The terpolymer will also contain an amount of magnesium oleate. Materials suitable for use as this layer are sold under the trade name DuPont® HPF™ AD 1027.

In yet another preferred embodiment, the centers/cores/layers comprise a copolymer comprising about 88% by weight of ethylene and about 12% by weight acrylic acid, with 100% of the acrylic acid neutralized by magnesium ions. The centers/cores/layers may also contain magnesium oleate. Material suitable for this embodiment was produced by DuPont as experimental product number SEP 1264-3. Preferably the centers/cores/layers are adjusted to a target specific gravity of 1.125 using inert fillers to adjust the density with minimal effect on the performance properties of the cover layer. Preferred fillers used for compounding the centers/cores/layers to the desired specific gravity include but are not limited to tungsten, zinc oxide, barium sulfate, and titanium dioxide.

A first set of intermediate layers were molded onto cores using DuPont® HPF™ AD1027, which is a terpolymer of

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about 73% to 74% ethylene, about 10.5% acrylic acid, and about 15.5% to 16.5% n-butyl acrylate, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the terpolymer contains a fixed amount of greater than 5 phr magnesium oleate. This material is compounded to a specific gravity of about 1.125 using barium sulfate and titanium dioxide. The Shore D hardness of this material (as measured on the curved surface of the inner cover layer) is about 58-60.

A second set of layers were molded onto each of the experimental cores using DuPont experimental HPF™ SEP 1264-3, which is a copolymer of about 88% ethylene and about 12% acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the copolymer contains a fixed amount of at least 5 phr magnesium oleate. This material is compounded to a specific gravity of about 1.125 using zinc oxide. The Shore D hardness of this material (as measured on the curved surface of the inner cover layer) is about 61-64.

A first set of covers were molded onto each of the core/layer components using DuPont HPF™ 1000, which is a terpolymer of about 75% to 76% ethylene, about 8.5% acrylic acid, and about 15.5% to 16.5% n-butyl acrylate, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the terpolymer contains a fixed amount of at least 5 phr of magnesium stearate. This material is compounded to a target specific gravity of about 1.125 using barium sulfate and titanium dioxide. The Shore D hardness of this material (as measured on the curved surface of the molded golf ball) is about 60-62.

In one embodiment, the formation of a golf ball starts with forming the inner core. The inner core, outer core, and the cover are formed by compression molding, by injection molding, or by casting. These methods of forming cores and covers of this type are well known in the art. The materials used for the inner and outer core, as well as the cover, are selected so that the desired playing characteristics of the ball are achieved. The inner and outer core materials have substantially different material properties so that there is a predetermined relationship between the inner and outer core materials, to achieve the desired playing characteristics of the ball.

In one embodiment, the inner core is formed of a first material having a first Shore D hardness, a first elastic modulus, a first specific gravity, and a first Bashore resilience. The outer core is formed of a second material having a second Shore D hardness, a second elastic modulus, a second specific gravity, and a second Bashore resilience. Preferably, the material property of the first material equals at least one selected from the group consisting of the first Shore D hardness differing from the second Shore D hardness by at least 10 points, the first elastic modulus differing from the second elastic modulus by at least 10%, the first specific gravity differing from the second specific gravity by at least 0.1, or a first Bashore resilience differing from the second Bashore resilience by at least 10%. It is more preferred that the first material have all of these material property relationships.

Moreover, it is preferred that the first material has the first Shore D hardness between about 30 and about 80, the first elastic modulus between about 5,000 psi and about 100,000 psi, the first specific gravity between about 0.8 and about 1.6, and the first Bashore resilience greater than 30%.

In another embodiment, the first Shore D hardness is less than the second Shore D hardness, the first elastic modulus is less than the second elastic modulus, the first specific gravity is less than the second specific gravity, and the first Bashore resilience is less than the second Bashore resilience. In another embodiment, the first material properties are greater than the second material properties. The relationship between

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the first and second material properties depends on the desired playability characteristics.

Suitable inner and outer core materials include HNP's neutralized with organic fatty acids and salts thereof, metal cations, or a combination of both, thermosets, such as rubber, polybutadiene, polyisoprene; thermoplastics, such as ionomer resins, polyamides or polyesters; or thermoplastic elastomers. Suitable thermoplastic elastomers include PEBAX®, HYTREL®, thermoplastic urethane, and KRATON®, which are commercially available from Elf-Atochem, DuPont, BF Goodrich, and Shell, respectively. The inner and outer core materials can also be formed from a castable material. Suitable castable materials include, but are not limited to, urethane, urea, epoxy, diols, or curatives.

The cover is selected from conventional materials used as golf ball covers based on the desired performance characteristics. The cover may be comprised of one or more layers. Cover materials such as ionomer resins, blends of ionomer resins, thermoplastic or thermoset urethanes, and balata, can be used as known in the art and discussed above. In other embodiments, additional layers may be added to those mentioned above or the existing layers may be formed by multiple materials.

When the core is formed with a fluid-filled center, the center is formed first then the inner core is molded around the center. Conventional molding techniques can be used for this operation. Then the outer core and cover are formed thereon, as discussed above. The fluid within the inner core can be a wide variety of materials including air, water solutions, liquids, gels, foams, hot-melts, other fluid materials and combinations thereof. The fluid is varied to modify the performance parameters of the ball, such as the moment of inertia or the spin decay rate. Examples of suitable liquids include either solutions such as salt in water, corn syrup, salt in water and corn syrup, glycol and water or oils. The liquid can further include pastes, colloidal suspensions, such as clay, barytes, carbon black in water or other liquid, or salt in water/glycol mixtures. Examples of suitable gels include water gelatin gels, hydrogels, water/methyl cellulose gels and gels comprised of copolymer rubber based materials such as styrene-butadiene-styrene rubber and paraffinic and/or naphthenic oil. Examples of suitable melts include waxes and hot melts. Hot-melts are materials which at or about normal room temperatures are solid but at elevated temperatures become liquid. A high melting temperature is desirable since the liquid core is heated to high temperatures during the molding of the inner core, outer core, and the cover. The liquid can be a reactive liquid system, which combines to form a solid. Examples of suitable reactive liquids are silicate gels, agar gels, peroxide cured polyester resins, two part epoxy resin systems and peroxide cured liquid polybutadiene rubber compositions.

The "effective compression constant," which is designated EC, is the ratio of deflection of a 1.50 inch diameter sphere made of any single material used in the core under a 100 kg load that as represented by the formula $EC = F/d$, where, F is a 100 kg load; and d is the deflection in millimeters. If the sphere tested is only inner core material, the effective compression constant for the inner core material alone is designated EC_{IC} . If the sphere tested is only outer core material, the effective compression constant for the outer core material alone is designated EC_{OC} . The sum of the constants for the inner core EC_{IC} and outer core EC_{OC} is the constant EC_S . If the sphere tested is inner and outer core material, the core effective compression constant is designated EC_C . It has been determined that very favorable cores are formed when their core effective compression constant EC_C is less than the

sum of the effective compression constants of the inner core and outer core EC_S . It is recommended that the core effective compression constant EC_C is less than about 90% of the sum of the effective compression constants of the inner core and outer core EC_S . More preferably, the core effective compression constant EC_C is less than or equal to about 50% of the sum of the effective compression constants of the inner core and outer core EC_S . The ratios of the inner core material to outer core material and the geometry of the inner core to the outer core are selected to achieve these core effective compression constants.

The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball cured polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D.

In addition to the HNP's neutralized with organic fatty acids and salts thereof, core compositions may comprise at least one rubber material having a resilience index of at least about 40. Preferably the resilience index is at least about 50. Polymers that produce resilient golf balls and, therefore, are suitable for the present invention, include but are not limited to CB23, CB22, commercially available from Bayer Corp. of Orange, Tex., BR60, commercially available from Enichem of Italy, and 1207G, commercially available from Goodyear Corp. of Akron, Ohio.

Additionally, the unvulcanized rubber, such as polybutadiene, in golf balls prepared according to the invention typically has a Mooney viscosity of between about 40 and about 80, more preferably, between about 45 and about 65, and most preferably, between about 45 and about 55. Mooney viscosity is typically measured according to ASTM-D1646.

When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 500 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-D2240, less than about 45 Shore D, preferably less than about 40 Shore D, more preferably between about 25 and about 40 Shore D, and most preferably between about 30 and about 40 Shore D. The casing preferably has a material hardness of less than about 70 Shore D, more preferably between about 30 and about 70 Shore D, and most preferably, between about 50 and about 65 Shore D.

In a preferred embodiment, the intermediate layer material hardness is between about 40 and about 70 Shore D and the outer cover layer material hardness is less than about 40 Shore D. In a more preferred embodiment, a ratio of the intermediate layer material hardness to the outer cover layer material hardness is greater than 1.5.

It should be understood, especially to one of ordinary skill in the art, that there is a fundamental difference between "material hardness" and "hardness, as measured directly on a golf ball." Material hardness is defined by the procedure set forth in ASTM-D2240 and generally involves measuring the hardness of a flat "slab" or "button" formed of the material of which the hardness is to be measured. Hardness, when mea-

sured directly on a golf ball (or other spherical surface) is a completely different measurement and, therefore, results in a different hardness value. This difference results from a number of factors including, but not limited to, ball construction (i.e., core type, number of core and/or cover layers, etc.), ball (or sphere) diameter, and the material composition of adjacent layers. It should also be understood that the two measurement techniques are not linearly related and, therefore, one hardness value cannot easily be correlated to the other.

In one embodiment, the core of the present invention has an Atti compression of between about 50 and about 90, more preferably, between about 60 and about 85, and most preferably, between about 65 and about 85. The overall outer diameter ("OD") of the core is less than about 1.590 inches, preferably, no greater than 1.580 inches, more preferably between about 1.540 inches and about 1.580 inches, and most preferably between about 1.525 inches to about 1.570 inches. The OD of the casing of the golf balls of the present invention is preferably between 1.580 inches and about 1.640 inches, more preferably between about 1.590 inches to about 1.630 inches, and most preferably between about 1.600 inches to about 1.630 inches.

Additionally, the core may be a two- or three-piece core, wherein the outermost core layer is formed from an HNP composition. In a two-piece core embodiment, the center or innermost core layer has a diameter of about 1.00 inches to about 1.60 inches, preferably about 1.20 inches to about 1.58 inches, more preferably about 1.30 inches to about 1.56 inches, and most preferably about 1.40 inches to about 1.55 inches. The outermost core layer (comprising the HNP composition) typically has a thickness of about 0.010 inches to about 0.250 inches, preferably about 0.020 inches to about 0.150 inches, more preferably about 0.040 inches to about 0.125 inches, and most preferably about 0.050 inches to about 0.095 inches.

In a three-piece core embodiment, the center or innermost core layer has a diameter of about 0.25 inches to about 1.50 inches, preferably about 0.50 inches to about 1.40 inches, more preferably about 0.75 inches to about 1.30 inches, and most preferably about 1.0 inches to about 1.20 inches. The intermediate core layer (between the innermost core layer (or center) and the outer core layer) typically has a thickness of about 0.050 inches to about 0.550 inches, preferably about 0.100 inches to about 0.300 inches, more preferably about 0.125 inches to about 0.290 inches, and most preferably about 0.200 inches to about 0.275 inches. The outermost core layer (comprising HNP) typically has a thickness of about 0.010 inches to about 0.250 inches, preferably about 0.020 inches to about 0.150 inches, more preferably about 0.040 inches to about 0.125 inches, and most preferably about 0.050 inches to about 0.095 inches.

In a preferred embodiment, the innermost core (center) has an outer surface hardness that is at least 5 Shore C less than the hardness of both the inner and outer surfaces of the outer core layer, preferably at least 7 Shore C less, most preferably at least 9 Shore C less.

The inner core surface hardness typically ranges from about 50 Shore C to about 96 Shore C; preferably about 57 Shore C to about 89 Shore C; more preferably about 63 Shore C to about 82 Shore C; most preferably about 63 Shore C, 67 Shore C, 71 Shore C, 75 Shore C, or 79 Shore C. The outer core surface hardness typically ranges from about 57 Shore C to about 100 Shore C; preferably about 63 Shore C to about 96 Shore C; more preferably about 70 Shore C to about 89 Shore C; and most preferably about 70 Shore C, 74 Shore C, 81 Shore C, 82 Shore C, or 86 Shore C.

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In a preferred embodiment, the innermost core (center) has an outer surface hardness that is at least 3 Shore D less than the hardness of both the inner and outer surfaces of the outer core layer, preferably at least 5 Shore D less, more preferably at least 7 Shore D less.

The inner core surface hardness typically ranges from about 30 Shore D to about 65 Shore D; preferably about 35 Shore D to about 60 Shore D; more preferably about 40 Shore D to about 55 Shore D; most preferably about 40 Shore D, 43 Shore D, 46 Shore D, 49 Shore D, or 52 Shore D. The outer core surface hardness typically ranges from about 35 Shore D to about 70 Shore D; preferably about 40 Shore D to about 65 Shore D; more preferably about 45 Shore D to about 60 Shore D; and most preferably about 45 Shore D, 48 Shore D, 51 Shore D, 54 Shore D, or 57 Shore D.

The present multilayer golf ball can have an overall diameter of any size. Although the USGA specifications limit the minimum size of a competition golf ball to 1.680 inches. There is no specification as to the maximum diameter. Golf balls of any size, however, can be used for recreational play. The preferred diameter of the present golf balls is from about 1.680 inches to about 1.800 inches. The more preferred diameter is from about 1.680 inches to about 1.760 inches. The most preferred diameter is about 1.680 inches to about 1.740 inches.

The golf balls of the present invention should have a moment of inertia ("MOI") of less than about 85 and, preferably, less than about 83. The MOI is typically measured on model number MOI-005-104 MOI Instrument manufactured by Inertia Dynamics of Collinsville, Conn. The instrument is plugged into a PC for communication via a COMM port and is driven by MOI Instrument Software version #1.2. U.S. Pat. Nos. 6,193,619; 6,207,784; 6,221,960; 6,414,082; 6,476,130; and 6,287,638 are incorporated in their entirety herein by express reference thereto. The highly-neutralized polymers of the present invention may also be used in golf equipment, in particular, inserts for golf clubs, such as putters, irons, and woods, and in golf shoes and components thereof.

As used herein, the term "about," used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range. Other than in the operating examples, or unless otherwise expressly specified, all of the numerical ranges, amounts, values and percentages such as those for amounts of materials, and others in the specification may be read as if prefaced by the word "about" even though the term "about" may not expressly appear with the value, amount or range. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Furthermore, when numerical ranges

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of varying scope are set forth herein, it is contemplated that any combination of these values inclusive of the recited values may be used. The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended solely as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball comprising:

an inner core layer comprising a thermoset rubber composition and having a first surface hardness;

a thermoplastic outer core layer having a second surface hardness, an inner surface hardness, and comprising a copolymer of ethylene and an α,β -unsaturated carboxylic acid, an organic acid or salt thereof, and sufficient cation source to fully-neutralize the acid groups of the copolymer;

an inner cover layer; and

an outer cover layer;

wherein the first surface hardness is less than the second surface hardness by at least 5 Shore C and less than the inner surface hardness by at least 5 Shore C.

2. The golf ball of claim 1, wherein the cation source is selected from a group consisting of metal cations of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, and aluminum.

3. The golf ball of claim 1, wherein the organic acid salt comprises an organic acid selected from the group consisting of aliphatic organic acids, aromatic organic acids, saturated mono- or multi-functional organic acids, unsaturated mono- or multi-functional organic acids, and multi-unsaturated mono- or multi-functional organic acids.

4. The golf ball of claim 1, wherein the organic acid comprises stearic acid, behenic acid, erucic acid, oleic acid, linoleic acid or dimerized derivatives thereof.

5. The golf ball of claim 1, wherein the organic acid salt comprises a cation selected from the group consisting of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, and calcium.

6. The golf ball of claim 1, wherein the outer cover is a castable polyurea or polyurethane.

7. The golf ball of claim 1, wherein the inner cover layer comprises a polyurethane, a polyurea, a polyurethane-urea hybrid, a polyurea-urethane hybrid, or an ionomer.

8. The golf ball of claim 1, wherein the inner core has a diameter of 0.8 inches to 1.4 inches.

9. The golf ball of claim 1, wherein the thermoplastic outer core layer has a thickness of 0.040 inches or greater.

10. The golf ball of claim 9, wherein the thermoplastic outer core layer has a thickness of 0.090 inches to 0.180 inches.

11. The golf ball of claim 1, wherein the first surface hardness is less than the second surface hardness by at least 7 Shore C and less than the inner surface hardness by at least 7 Shore C.

* * * * *

Exhibit C

(12) **United States Patent**
Sullivan et al.(10) **Patent No.:** **US 8,123,632 B2**
(45) **Date of Patent:** ***Feb. 28, 2012**(54) **MULTI-LAYER GOLF BALL**(75) Inventors: **Michael J. Sullivan**, Barrington, RI (US); **Derek A. Ladd**, Acushnet, MA (US); **William E. Morgan**, Barrington, RI (US); **Herbert C. Boehm**, Norwell, MA (US)(73) Assignee: **Acushnet Company**, Fairhaven, MA (US)(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.
This patent is subject to a terminal disclaimer.(21) Appl. No.: **13/024,901**(22) Filed: **Feb. 10, 2011**(65) **Prior Publication Data**

US 2011/0130221 A1 Jun. 2, 2011

Related U.S. Application Data

(63) Continuation of application No. 12/233,776, filed on Sep. 19, 2008, now Pat. No. 7,887,437, which is a continuation-in-part of application No. 12/048,003, filed on Mar. 13, 2008, which is a continuation-in-part of application No. 11/767,070, filed on Jun. 22, 2007, now abandoned, which is a continuation-in-part of application No. 10/773,906, filed on Feb. 6, 2004, now Pat. No. 7,255,656, which is a continuation-in-part of

application No. 10/341,574, filed on Jan. 13, 2003, now Pat. No. 6,852,044, which is a continuation-in-part of application No. 10/002,641, filed on Nov. 28, 2001, now Pat. No. 6,547,677.

(51) **Int. Cl.**
A63B 37/06 (2006.01)
(52) **U.S. Cl.** **473/376**
(58) **Field of Classification Search** **473/376**
See application file for complete search history.(56) **References Cited**

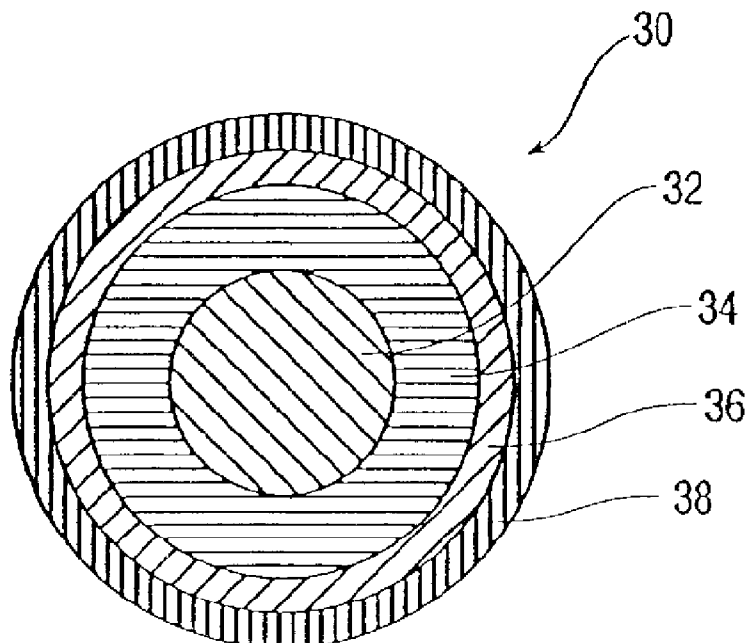
U.S. PATENT DOCUMENTS

5,782,707	A	7/1998	Yamagishi et al.
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6,987,159	B2	1/2006	Iwami
7,086,969	B2	8/2006	Higuchi et al.
7,153,224	B2	12/2006	Higuchi et al.
7,175,542	B2	2/2007	Watanabe et al.
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Primary Examiner — Raeann Gorden(74) *Attorney, Agent, or Firm* — Mandi B. Milbank(57) **ABSTRACT**

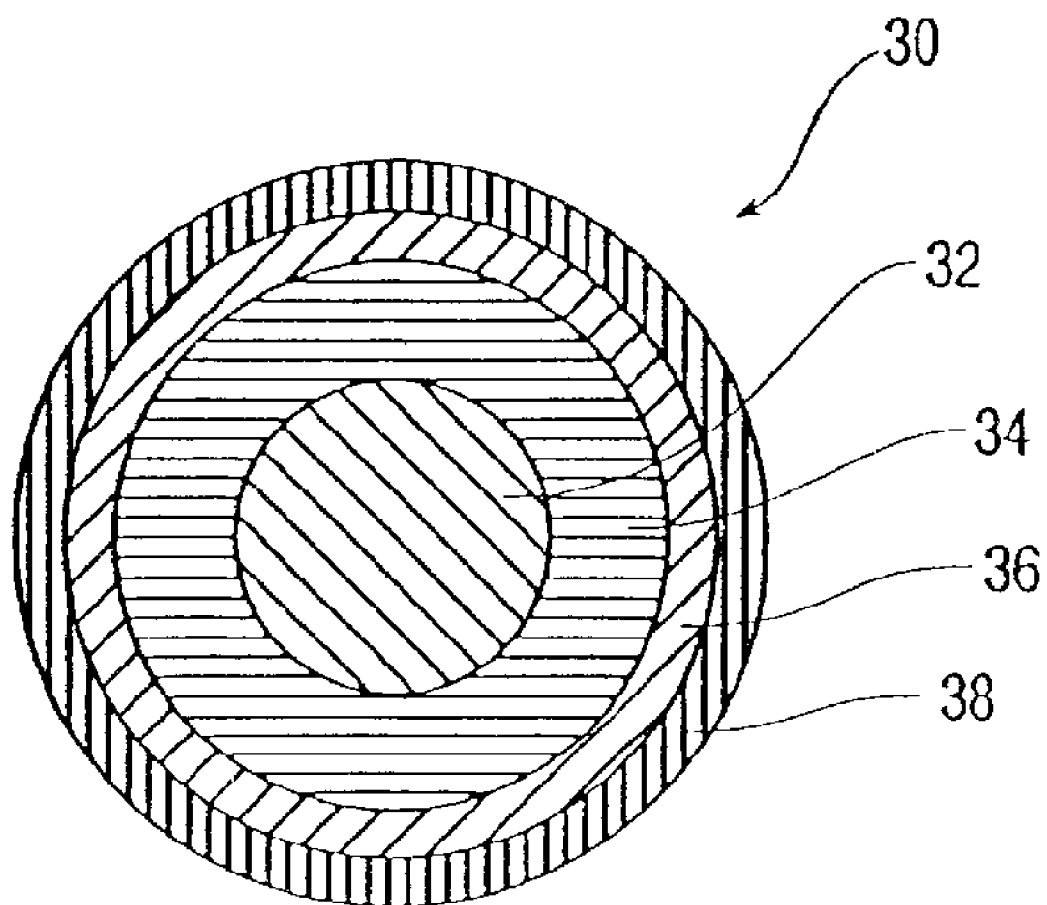
Golf balls consisting of a dual core and a dual cover are disclosed. The dual core consists of an inner core layer formed from a rubber composition and an outer core layer formed from a highly neutralized polymer composition.

24 Claims, 1 Drawing Sheet

U.S. Patent

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MULTI-LAYER GOLF BALL**CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is a continuation of U.S. patent application Ser. No. 12/233,776, filed Sep. 19, 2008, which is a continuation-in-part of U.S. patent application Ser. No. 12/048,003, filed Mar. 13, 2008, which is a continuation-in-part of U.S. patent application Ser. No. 11/767,070, filed Jun. 22, 2007, which is a continuation-in-part of U.S. patent application Ser. No. 10/773,906, filed Feb. 6, 2004, now U.S. Pat. No. 7,255,656, which is a continuation-in-part of U.S. patent application Ser. No. 10/341,574, filed Jan. 13, 2003, now U.S. Pat. No. 6,852,044, which is a continuation-in-part of U.S. patent application Ser. No. 10/002,641, filed Nov. 28, 2001, now U.S. Pat. No. 6,547,677. The entire disclosure of each of these references is hereby incorporated herein by reference.

FIELD OF THE INVENTION

The present invention generally relates to golf balls, and more particularly to golf balls having dual cores surrounded by dual covers, wherein the outer surface hardness of the outer core layer is greater than the material hardness of the inner cover layer.

BACKGROUND OF THE INVENTION

Numerous golf balls having a multilayer construction wherein the core hardness and cover hardness have been variously improved are disclosed in the prior art. For example, U.S. Pat. No. 6,987,159 to Iwami discloses a solid golf ball with a solid core and a polyurethane cover, wherein the difference in Shore D hardness between a center portion and a surface portion of the solid core is at least 15, the polyurethane cover has a thickness (t) of not more than 1.0 mm and is formed from a cured urethane composition having a Shore D hardness (D) of from 35 to 60, and a product of t and D ranges from 10 to 45.

U.S. Pat. No. 7,175,542 to Watanabe et al. discloses a multi-piece solid golf ball composed of a multilayer core having at least an inner core layer and an outer core layer, one or more cover layers which enclose the core, and numerous dimples formed on a surface of the cover layer. The golf ball is characterized in that the following hardness conditions are satisfied:

- (1) $(\text{JIS-C hardness of cover}) - (\text{JIS-C hardness at center of core}) \geq 27$, (2) $23 \leq (\text{JIS-C hardness at surface of core}) - (\text{JIS-C hardness at center of core}) \leq 40$, and (3) $0.50 \leq [(\text{deflection amount of entire core}) / (\text{deflection amount of inner core layer})] \leq 0.75$.

U.S. Pat. No. 6,679,791 to Watanabe discloses a multi-piece golf ball which includes a rubbery elastic core, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer between the core and the cover. The intermediate layer is composed of a resin material which is harder than the cover. The elastic core has a hardness which gradually increases radially outward from the center to the surface thereof. The center and surface of the elastic core have a hardness difference of at least 18 JIS-C hardness units.

U.S. Pat. No. 5,782,707 to Yamagishi et al. discloses a three-piece solid golf ball consisting of a solid core, an intermediate layer, and a cover, wherein the hardness is measured by a JIS-C scale hardness meter, the core center hardness is up to 75 degrees, the core surface hardness is up to 85 degrees, the core surface hardness is higher than the core center hard-

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ness by 8 to 20 degrees, the intermediate layer hardness is higher than the core surface hardness by at least 5 degrees, and the cover hardness is lower than the intermediate layer hardness by at least 5 degrees.

Additional examples can be found, for example, in U.S. Pat. Nos. 6,686,436 to Iwami, 6,786,836 to Higuchi et al., 7,086,969 to Higuchi et al., 7,153,224 to Higuchi et al., and 7,226,367 to Higuchi et al.

The present invention provides a novel multilayer golf ball construction which provides desirable spin and distance properties.

SUMMARY OF THE INVENTION

In one embodiment, the present invention is directed to a golf ball consisting of an inner core layer, an outer core layer, an inner cover layer, and an outer cover layer. The inner core layer is formed from a rubber composition and has a diameter of from 1.200 inches to 1.300 inches, a center hardness (H_{center}) of 50 Shore C or greater, and an outer surface hardness of 65 Shore C or greater. The outer core layer is formed from a highly neutralized polymer composition and has an outer surface hardness ($H_{outer\ core}$) of 75 Shore C or greater. The inner cover layer is formed from a thermoplastic composition and has a material hardness ($H_{inner\ cover}$) less than the outer surface hardness of the outer core layer. The outer cover layer is formed from a composition selected from the group consisting of polyurethanes, polyureas, and copolymers and blends thereof.

In another embodiment, the present invention is directed to a golf ball comprising a core and a cover. The core consists of an inner core layer and an outer core layer. The inner core layer is formed from a rubber composition and has a diameter of from 1.200 inches to 1.300 inches, a center hardness (H_{center}) of from 50 Shore C to 70 Shore C, and an outer surface hardness of from 60 Shore C to 85 Shore C. The outer core layer is formed from a highly neutralized polymer composition and has an outer surface hardness ($H_{outer\ core}$) of from 80 Shore C to 95 Shore C. The cover consists of an inner cover layer and an outer cover layer. The inner cover layer is formed from a thermoplastic composition and has a material hardness ($H_{inner\ cover}$) less than the outer surface hardness of the outer core layer. The outer cover layer is formed from a composition selected from the group consisting of polyurethanes, polyureas, and copolymers and blends thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a golf ball according to an embodiment of the present invention.

DETAILED DESCRIPTION

FIG. 1 shows a golf ball 30 according to an embodiment of the present invention, including an inner core layer 32, an outer core layer 34, an inner cover layer 36, and an outer cover layer 38.

A golf ball having a dual core (i.e., two-layer core) and a dual cover (i.e., two-layer cover) enclosing the core is disclosed. The dual core consists of an inner core layer and an outer core layer. The inner core layer has a diameter within a range having a lower limit of 0.750 or 1.000 or 1.100 or 1.200 inches and an upper limit of 1.300 or 1.350 or 1.400 inches. The outer core layer encloses the inner core layer such that the two-layer core has an overall diameter within a range having a lower limit of 1.400 or 1.500 or 1.510 or 1.520 or 1.525 inches and an upper limit of 1.540 or 1.550 or 1.555 or 1.560

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or 1.590 inches. In a particular embodiment, the inner core layer has a diameter of 1.250 inches and the outer core layer encloses the inner core layer such that the two-layer core has an overall diameter of 1.530 inches or 1.550 inches.

The inner core layer has a center hardness (H_{center}) of 45 Shore C or greater, or 50 Shore C or greater, or 55 Shore C or greater, or 60 Shore C or greater, or a center hardness within a range having a lower limit of 40 or 45 or 50 or 55 or 60 Shore C and an upper limit of 65 or 70 or 75 or 80 Shore C. The inner core layer has an outer surface hardness of 65 Shore C or greater, or 70 Shore C or greater, or 75 Shore C or greater, or 80 Shore C or greater, or an outer surface hardness within a range having a lower limit of 55 or 60 or 65 or 70 or 75 Shore C and an upper limit of 80 or 85 or 90 Shore C. In a particular embodiment, the Shore C hardness of the inner core layer's outer surface is greater than or equal to the center Shore C hardness. In another particular embodiment, the inner core layer has a positive hardness gradient wherein the Shore C hardness of the inner core layer's outer surface is at least 10 Shore C units greater, or at least 15 Shore C units greater, or 19 Shore C units greater than the center Shore C hardness.

The outer core layer has an outer surface hardness ($H_{outer\ core}$) of 75 Shore C or greater, or 80 Shore C or greater, or greater than 80 Shore C, or 85 Shore C or greater, or greater than 85 Shore C, or 87 Shore C or greater, or greater than 87 Shore C, or 89 Shore C or greater, or greater than 89 Shore C, or 90 Shore C or greater, or greater than 90 Shore C, or an outer surface hardness within a range having a lower limit of 75 or 80 or 85 or 90 Shore C and an upper limit of 95 Shore C. In a particular embodiment, the overall dual core has a positive hardness gradient wherein the Shore C hardness of the outer core layer's outer surface is at least 20 Shore C units greater, or at least 25 Shore C units greater, or at least 30 Shore C units greater, than the inner core layer's center Shore C hardness. In another particular embodiment, the Shore C hardness of the outer core layer's outer surface is greater than the material hardness of the inner cover layer.

For purposes of the present disclosure, the center hardness of the inner core layer is obtained according to the following procedure. The core is gently pressed into a hemispherical holder having an internal diameter approximately slightly smaller than the diameter of the core, such that the core is held in place in the hemispherical portion of the holder while concurrently leaving the geometric central plane of the core exposed. The core is secured in the holder by friction, such that it will not move during the cutting and grinding steps, but the friction is not so excessive that distortion of the natural shape of the core would result. The core is secured such that the parting line of the core is roughly parallel to the top of the holder. The diameter of the core is measured 90 degrees to this orientation prior to securing. A measurement is also made from the bottom of the holder to the top of the core to provide a reference point for future calculations. A rough cut is made slightly above the exposed geometric center of the core using a band saw or other appropriate cutting tool, making sure that the core does not move in the holder during this step. The remainder of the core, still in the holder, is secured to the base plate of a surface grinding machine. The exposed 'rough' surface is ground to a smooth, flat surface, revealing the geometric center of the core, which can be verified by measuring the height from the bottom of the holder to the exposed surface of the core, making sure that exactly half of the original height of the core, as measured above, has been removed to within ± 0.004 inches. Leaving the core in the holder, the center of the core is found with a center square and carefully marked and the hardness is measured at the center mark according to ASTM D-2240. Additional hardness mea-

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surements at any distance from the center of the core can then be made by drawing a line radially outward from the center mark, and measuring the hardness at any given distance along the line, typically in 2 mm increments from the center. The hardness at a particular distance from the center should be measured along at least two, preferably four, radial arms located 180° apart, or 90° apart, respectively, and then averaged. All hardness measurements performed on a plane passing through the geometric center are performed while the core is still in the holder and without having disturbed its orientation, such that the test surface is constantly parallel to the bottom of the holder, and thus also parallel to the properly aligned foot of the durometer.

For purposes of the present disclosure, the outer surface hardness of a golf ball layer is measured on the actual outer surface of the layer and is obtained from the average of a number of measurements taken from opposing hemispheres, taking care to avoid making measurements on the parting line of the core or on surface defects, such as holes or protrusions. Hardness measurements are made pursuant to ASTM D-2240 "Indentation Hardness of Rubber and Plastic by Means of a Durometer." Because of the curved surface, care must be taken to insure that the golf ball or golf ball subassembly is centered under the durometer indenter before a surface hardness reading is obtained. A calibrated, digital durometer, capable of reading to 0.1 hardness units is used for all hardness measurements and is set to take hardness readings at 1 second after the maximum reading is obtained. The digital durometer must be attached to, and its foot made parallel to, the base of an automatic stand. The weight on the durometer and attack rate conform to ASTM D-2240.

For purposes of the present disclosure, a hardness gradient of a golf ball layer is defined by hardness measurements made at the outer surface of the layer and the inner surface of the layer. "Negative" and "positive" refer to the result of subtracting the hardness value at the innermost surface of the golf ball component from the hardness value at the outermost surface of the component. For example, if the outer surface of a solid core has a lower hardness value than the center (i.e., the surface is softer than the center), the hardness gradient will be deemed a "negative" gradient.

Thermoplastic layers of golf balls disclosed herein may be treated in such a manner as to create a positive or negative hardness gradient, as disclosed, for example, in U.S. patent application Ser. Nos. 11/939,632, filed Nov. 14, 2007; 11/939,634, filed Nov. 14, 2007; 11/939,635, filed Nov. 14, 2007; and 11/939,637 filed Nov. 14, 2007. The entire disclosure of each of these references is hereby incorporated herein by reference. In golf ball layers of the present invention wherein a thermosetting rubber is used, gradient-producing processes and/or gradient-producing rubber formulations may be employed, as disclosed, for example, in U.S. patent application Ser. Nos. 12/048,665, filed Mar. 14, 2008; 11/829,461, filed Jul. 27, 2007; 11/772,903, filed Jul. 3, 2007; 11/832,163, filed Aug. 1, 2007; and U.S. Pat. No. 7,410,429. The entire disclosure of each of these references is hereby incorporated herein by reference.

The inner core layer is preferably formed from a rubber composition. Suitable rubber compositions include natural and synthetic rubbers including, but not limited to, polybutadiene, polyisoprene, ethylene propylene rubber ("EPR"), styrene-butadiene rubber, styrenic block copolymer rubbers (such as SI, SIS, SB, SBS, SIBS, and the like, where "S" is styrene, "I" is isobutylene, and "B" is butadiene), butyl rubber, halobutyl rubber, polystyrene elastomers, polyethylene elastomers, polyurethane elastomers, polyurea elastomers, metallocene-catalyzed elastomers and plastomers, copoly-

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mers of isobutylene and para-alkylstyrene, halogenated copolymers of isobutylene and para-alkylstyrene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and combinations of two or more thereof. Diene rubbers are preferred, particularly polybutadiene, styrene-butadiene, and mixtures of polybutadiene with other elastomers wherein the amount of polybutadiene present is at least 40 wt % based on the total polymeric weight of the mixture. Suitable polybutadiene-based and styrene-butadiene-based rubber core compositions preferably comprise the base rubber, an initiator agent, and a coagent. Suitable examples of commercially available polybutadienes include, but are not limited to, Buna CB neodymium catalyzed polybutadiene rubbers, such as Buna CB 23, and Taktene® cobalt catalyzed polybutadiene rubbers, such as Taktene® 220 and 221, commercially available from LANXESS® Corporation; SE BR-1220, commercially available from The Dow Chemical Company; Europrene® NEO-CIS® BR 40 and BR 60, commercially available from Polimeri Europa®; UBEPOL-BR® rubbers, commercially available from UBE Industries, Inc.; BR 01, commercially available from Japan Synthetic Rubber Co., Ltd.; and Neodene neodymium catalyzed high cis polybutadiene rubbers, such as Neodene BR 40, commercially available from Karbochem.

Suitable initiator agents include organic peroxides, high energy radiation sources capable of generating free radicals, and combinations thereof. High energy radiation sources capable of generating free radicals include, but are not limited to, electron beams, ultra-violet radiation, gamma radiation, X-ray radiation, infrared radiation, heat, and combinations thereof. Suitable organic peroxides include, but are not limited to, dicumyl peroxide; n-butyl-4,4-di(t-butylperoxy) valerate; 1,1-di(t-butylperoxy)3,3,5-trimethylcyclohexane; 2,5-dimethyl-2,5-di(t-butylperoxy) hexane; di-t-butyl peroxide; di-t-amyl peroxide; t-butyl peroxide; t-butyl cumyl peroxide; 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3; di(2-t-butylperoxyisopropyl)benzene; dilauroyl peroxide; dibenzoyl peroxide; t-butyl hydroperoxide; lauryl peroxide; benzoyl peroxide; and combinations thereof. In a particular embodiment, the initiator agent is dicumyl peroxide, including, but not limited to Perkadox® BC, commercially available from Akzo Nobel. Peroxide initiator agents are generally present in the rubber composition in an amount of at least 0.05 parts by weight per 100 parts of the base rubber, or an amount within the range having a lower limit of 0.05 parts or 0.1 parts or 1 part or 1.25 parts or 1.5 parts by weight per 100 parts of the base rubber, and an upper limit of 2.5 parts or 3 parts or 5 parts or 6 parts or 10 parts or 15 parts by weight per 100 parts of the base rubber.

Coagents are commonly used with peroxides to increase the state of cure. Suitable coagents include, but are not limited to, metal salts of unsaturated carboxylic acids; unsaturated vinyl compounds and polyfunctional monomers (e.g., trimethylolpropane trimethacrylate); phenylene bismaleimide; and combinations thereof. Particular examples of suitable metal salts include, but are not limited to, one or more metal salts of acrylates, diacrylates, methacrylates, and dimethacrylates, wherein the metal is selected from magnesium, calcium, zinc, aluminum, lithium, nickel, and sodium. In a particular embodiment, the coagent is selected from zinc salts of acrylates, diacrylates, methacrylates, dimethacrylates, and mixtures thereof. In another particular embodiment, the coagent is zinc diacrylate. When the coagent is zinc diacrylate and/or zinc dimethacrylate, the coagent is typically included in the rubber composition in an amount within the range

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having a lower limit of 1 or 5 or 10 or 15 or 19 or 20 parts by weight per 100 parts of the base rubber, and an upper limit of 24 or 25 or 30 or 35 or 40 or 45 or 50 or 60 parts by weight per 100 parts of the base rubber. When one or more less active coagents are used, such as zinc monomethacrylate and various liquid acrylates and methacrylates, the amount of less active coagent used may be the same as or higher than for zinc diacrylate and zinc dimethacrylate coagents. The desired compression may be obtained by adjusting the amount of crosslinking, which can be achieved, for example, by altering the type and amount of coagent.

The rubber composition optionally includes a curing agent. Suitable curing agents include, but are not limited to, sulfur; N-oxydiethylene 2-benzothiazole sulfenamide; N,N-diortho-tolylguanidine; bismuth dimethyldithiocarbamate; N-cyclohexyl 2-benzothiazole sulfenamide; N,N-diphenylguanidine; 4-morpholinyl-2-benzothiazole disulfide; dipentamethylenethiuram hexasulfide; thiuram disulfides; mercaptobenzothiazoles; sulfenamides; dithiocarbamates; thiuram sulfides; guanidines; thioureas; xanthates; dithiophosphates; aldehyde-amines; dibenzothiazyl disulfide; tetraethylthiuram disulfide; tetrabutylthiuram disulfide; and combinations thereof.

The rubber composition optionally contains one or more antioxidants. Antioxidants are compounds that can inhibit or prevent the oxidative degradation of the rubber. Some antioxidants also act as free radical scavengers; thus, when antioxidants are included in the rubber composition, the amount of initiator agent used may be as high or higher than the amounts disclosed herein. Suitable antioxidants include, for example, dihydroquinoline antioxidants, amine type antioxidants, and phenolic type antioxidants.

The rubber composition may contain one or more fillers to adjust the density and/or specific gravity of the core. Exemplary fillers include precipitated hydrated silica, clay, talc, asbestos, glass fibers, aramid fibers, mica, calcium metasilicate, zinc sulfate, barium sulfate, zinc sulfide, lithopone, silicates, silicon carbide, diatomaceous earth, polyvinyl chloride, carbonates (e.g., calcium carbonate, zinc carbonate, barium carbonate, and magnesium carbonate), metals (e.g., titanium, tungsten, aluminum, bismuth, nickel, molybdenum, iron, lead, copper, boron, cobalt, beryllium, zinc, and tin), metal alloys (e.g., steel, brass, bronze, boron carbide whiskers, and tungsten carbide whiskers), oxides (e.g., zinc oxide, tin oxide, iron oxide, calcium oxide, aluminum oxide, titanium dioxide, magnesium oxide, and zirconium oxide), particulate carbonaceous materials (e.g., graphite, carbon black, cotton flock, natural bitumen, cellulose flock, and leather fiber), microballoons (e.g., glass and ceramic), fly ash, regrind (i.e., core material that is ground and recycled), nanofillers and combinations thereof. The amount of particulate material(s) present in the rubber composition is typically within a range having a lower limit of 5 parts or 10 parts by weight per 100 parts of the base rubber, and an upper limit of 30 parts or 50 parts or 100 parts by weight per 100 parts of the base rubber. Filler materials may be dual-functional fillers, such as zinc oxide (which may be used as a filler/acid scavenger) and titanium dioxide (which may be used as a filler/brightener material).

The rubber composition may also contain one or more additives selected from processing aids, processing oils, plasticizers, coloring agents, fluorescent agents, chemical blowing and foaming agents, defoaming agents, stabilizers, softening agents, impact modifiers, free radical scavengers, accelerators, scorch retarders, and the like. The amount of additive(s) typically present in the rubber composition is typically within a range having a lower limit of 0 parts by weight

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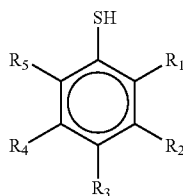
per 100 parts of the base rubber, and an upper limit of 20 parts or 50 parts or 100 parts or 150 parts by weight per 100 parts of the base rubber.

The rubber composition optionally includes a soft and fast agent. As used herein, "soft and fast agent" means any compound or a blend thereof that is capable of making a core 1) softer (have a lower compression) at a constant COR and/or 2) faster (have a higher COR) at equal compression, when compared to a core equivalently prepared without a soft and fast agent. Preferably, the rubber composition contains from 0.05 phr to 10.0 phr of a soft and fast agent. In one embodiment, the soft and fast agent is present in an amount within a range having a lower limit of 0.05 or 0.1 or 0.2 or 0.5 phr and an upper limit of 1.0 or 2.0 or 3.0 or 5.0 phr. In another embodiment, the soft and fast agent is present in an amount of from 2.0 phr to 5.0 phr, or from 2.35 phr to 4.0 phr, or from 2.35 phr to 3.0 phr. In an alternative high concentration embodiment, the soft and fast agent is present in an amount of from 5.0 phr to 10.0 phr, or from 6.0 phr to 9.0 phr, or from 7.0 phr to 8.0 phr. In another embodiment, the soft and fast agent is present in an amount of 2.6 phr.

Suitable soft and fast agents include, but are not limited to, organosulfur and metal-containing organosulfur compounds; organic sulfur compounds, including mono, di, and polysulfides, thiol, and mercapto compounds; inorganic sulfide compounds; blends of an organosulfur compound and an inorganic sulfide compound; Group VIA compounds; substituted and unsubstituted aromatic organic compounds that do not contain sulfur or metal; aromatic organometallic compounds; hydroquinones; benzoquinones; quinhydrones; catechols; resorcinols; and combinations thereof.

As used herein, "organosulfur compound" refers to any compound containing carbon, hydrogen, and sulfur, where the sulfur is directly bonded to at least 1 carbon. As used herein, the term "sulfur compound" means a compound that is elemental sulfur, polymeric sulfur, or a combination thereof. It should be further understood that the term "elemental sulfur" refers to the ring structure of S₈ and that "polymeric sulfur" is a structure including at least one additional sulfur relative to elemental sulfur.

Particularly suitable as soft and fast agents are organosulfur compounds having the following general formula:



where R₁-R₅ can be C₁-C₈ alkyl groups; halogen groups; thiol groups (—SH), carboxylated groups; sulfonated groups; and hydrogen; in any order; and also pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol;

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2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; zinc salts thereof; non-metal salts thereof, for example, ammonium salt of pentachlorothiophenol; magnesium pentachlorothiophenol; cobalt pentachlorothiophenol; and combinations thereof. Preferably, the halogenated thiophenol compound is pentachlorothiophenol, which is commercially available in neat form or under the tradename STRUKTOL®, a clay-based carrier containing the sulfur compound pentachlorothiophenol loaded at 45 percent (correlating to 2.4 parts PCTP). STRUKTOL® is commercially available from Struktol Company of America of Stow, Ohio. PCTP is commercially available in neat form from eChinacem of San Francisco, Calif. and in the salt form from eChinacem of San Francisco, Calif. Most preferably, the halogenated thiophenol compound is the zinc salt of pentachlorothiophenol, which is commercially available from eChinacem of San Francisco, Calif. Suitable organosulfur compounds are further disclosed, for example, in U.S. Pat. Nos. 6,635,716, 6,919,393, 7,005,479 and 7,148,279, the entire disclosures of which are hereby incorporated herein by reference.

Suitable metal-containing organosulfur compounds include, but are not limited to, cadmium, copper, lead, and tellurium analogs of diethyldithiocarbamate, diamyldithiocarbamate, and dimethyldithiocarbamate, and combinations thereof. Additional examples are disclosed in U.S. Pat. No. 7,005,479, the entire disclosure of which is hereby incorporated herein by reference.

Suitable disulfides include, but are not limited to, 4,4'-diphenyl disulfide; 4,4'-ditolyl disulfide; 2,2'-benzamido diphenyl disulfide; bis(2-aminophenyl) disulfide; bis(4-aminophenyl) disulfide; bis(3-aminophenyl) disulfide; 2,2'-bis(4-aminonaphthyl) disulfide; 2,2'-bis(3-aminonaphthyl) disulfide; 2,2'-bis(4-aminonaphthyl) disulfide; 2,2'-bis(5-aminonaphthyl) disulfide; 2,2'-bis(6-aminonaphthyl) disulfide; 2,2'-bis(7-aminonaphthyl) disulfide; 2,2'-bis(8-aminonaphthyl) disulfide; 1,1'-bis(2-aminonaphthyl) disulfide; 1,1'-bis(3-aminonaphthyl) disulfide; 1,1'-bis(3-aminonaphthyl) disulfide; 1,1'-bis(4-aminonaphthyl) disulfide; 1,1'-bis(5-aminonaphthyl) disulfide; 1,1'-bis(6-aminonaphthyl) disulfide; 1,1'-bis(7-aminonaphthyl) disulfide; 1,1'-bis(8-aminonaphthyl) disulfide; 1,2'-diamino-1,2'-dithiodinaphthalene; 2,3'-diamino-1,2'-dithiodinaphthalene; bis(4-chlorophenyl) disulfide; bis(2-chlorophenyl) disulfide; bis(3-chlorophenyl) disulfide; bis(4-bromophenyl) disulfide; bis(2-bromophenyl) disulfide; bis(3-bromophenyl) disulfide; bis(4-fluorophenyl) disulfide; bis(4-iodophenyl) disulfide; bis(2,5-dichlorophenyl) disulfide; bis(3,5-dichlorophenyl) disulfide; bis(2,4-dichlorophenyl) disulfide; bis(2,6-dichlorophenyl) disulfide; bis(2,5-dibromophenyl) disulfide; bis(3,5-dibromophenyl) disulfide; bis(2-chloro-5-bromophenyl) disulfide; bis(2,4,6-trichlorophenyl) disulfide; bis(2,3,4,5,6-pentachlorophenyl) disulfide; bis(4-cyanophenyl) disulfide; bis(2-cyanophenyl) disulfide; bis(4-nitrophenyl) disulfide; bis(2-nitrophenyl) disulfide; 2,2'-dithiobenzoic acid ethylester; 2,2'-dithiobenzoic acid methylester; 2,2'-dithiobenzoic acid; 4,4'-dithiobenzoic acid ethylester; bis(4-acetylphenyl) disulfide; bis(2-acetylphenyl) disulfide; bis(4-formylphenyl) disulfide; bis(4-carbamoylphenyl) disulfide; 1,1'-dinaphthyl disulfide; 2,2'-dinaphthyl disulfide; 1,2'-dinaphthyl disulfide;

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2,2'-bis(1-chlorodinaphthyl) disulfide; 2,2'-bis(1-bromonaphthyl) disulfide; 1,1'-bis(2-chloronaphthyl) disulfide; 2,2'-bis(1-cyanonaphthyl) disulfide; 2,2'-bis(1-acetylnaphthyl) disulfide; and the like; and combinations thereof.

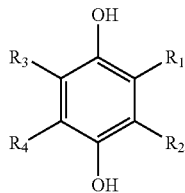
Suitable inorganic sulfide compounds include, but are not limited to, titanium sulfide, manganese sulfide, and sulfide analogs of iron, calcium, cobalt, molybdenum, tungsten, copper, selenium, yttrium, zinc, tin, and bismuth.

Suitable Group VIA compounds include, but are not limited to, elemental sulfur and polymeric sulfur, such as those which are commercially available from Elastochem, Inc. of Chardon, Ohio; sulfur catalyst compounds which include PB(RM-S)-80 elemental sulfur and PB(CRST)-65 polymeric sulfur, each of which is available from Elastochem, Inc; tellurium catalysts, such as TELLOY®, and selenium catalysts, such as VANDEX®, each of which is commercially available from RT Vanderbilt.

Suitable substituted and unsubstituted aromatic organic components that do not include sulfur or a metal include, but are not limited to, 4,4'-diphenyl acetylene, azobenzene, and combinations thereof. The aromatic organic group preferably ranges in size from C₆ to C₂₀, and more preferably from C₆ to C₁₀.

Suitable substituted and unsubstituted aromatic organometallic compounds include, but are not limited to, those having the formula (R₁)_x-R₃-M-R₄-(R₂)_y, wherein R₁ and R₂ are each hydrogen or a substituted or unsubstituted C₁₋₂₀ linear, branched, or cyclic alkyl, alkoxy, or alkylthio group, or a single, multiple, or fused ring C₆ to C₂₄ aromatic group; x and y are each an integer from 0 to 5; R₃ and R₄ are each selected from a single, multiple, or fused ring C₆ to C₂₄ aromatic group; and M includes an azo group or a metal component. Preferably, R₃ and R₄ are each selected from a C₆ to C₁₀ aromatic group, more preferably selected from phenyl, benzyl, naphthyl, benzamido, and benzothiazyl. Preferably R₁ and R₂ are each selected from substituted and unsubstituted C₁₋₁₀ linear, branched, and cyclic alkyl, alkoxy, and alkylthio groups, and C₆ to C₁₀ aromatic groups. When R₁, R₂, R₃, and R₄ are substituted, the substitution may include one or more of the following substituent groups: hydroxy and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carboxyl including esters, acids, and metal salts thereof; silyl; acrylates and metal salts thereof; sulfonyl and sulfonamide; and phosphates and phosphites. When M is a metal component, it may be any suitable elemental metal. The metal is generally a transition metal, and is preferably tellurium or selenium.

Suitable hydroquinones include, but are not limited to, compounds represented by the following formula, and hydrates thereof:

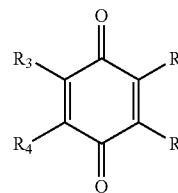


wherein each R₁, R₂, R₃, and R₄ is independently selected from the group consisting of hydrogen, a halogen group (F, Cl, Br, I), an alkyl group, a carboxyl group (—COOH) and metal salts thereof (e.g., —COO[−]M⁺) and esters thereof (—COOR), an acetate group (—CH₂COOH) and esters thereof (—CH₂COOR), a formyl group (—CHO), an acyl

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group (—COR), an acetyl group (—COCH₃), a halogenated carbonyl group (—COX), a sulfo group (—SO₃H) and esters thereof (—SO₃R), a halogenated sulfonyl group (—SO₂X), a sulfino group (—SO₂H), an alkylsulfinyl group (—SOR), a carbamoyl group (—CONH₂), a halogenated alkyl group, a cyano group (—CN), an alkoxy group (—OR), a hydroxy group (—OH) and metal salts thereof (e.g., —O[−]M⁺), an amino group (—NH₂), a nitro group (—NO₂), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl (—C(CH₃)₂phenyl); benzyl (—CH₂phenyl)], a nitroso group (—NO), an acetamido group (—NHCOCH₃), and a vinyl group (—CH=CH₂). Particularly preferred hydroquinones include compounds represented by the above formula, and hydrates thereof, wherein each R₁, R₂, R₃, and R₄ is independently selected from the group consisting of: a metal salt of a carboxyl group (e.g., —COO[−]M⁺), an acetate group (—CH₂COOH) and esters thereof (—CH₂COOR), a hydroxy group (—OH), a metal salt of a hydroxy group (e.g., —O[−]M⁺), an amino group (—NH₂), a nitro group (—NO₂), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl (—C(CH₃)₂phenyl); benzyl (—CH₂phenyl)], a nitroso group (—NO), an acetamido group (—NHCOCH₃), and a vinyl group (—CH=CH₂). Examples of particularly suitable hydroquinones include, but are not limited to, hydroquinone; tetrachlorohydroquinone; 2-chlorohydroquinone; 2-bromohydroquinone; 2,5-dichlorohydroquinone; 2,5-dibromohydroquinone; tetrabromohydroquinone; 2-methylhydroquinone; 2-t-butylhydroquinone; 2,5-di-t-amylhydroquinone; and 2-(2-chlorophenyl) hydroquinone hydrate. Hydroquinone and tetrachlorohydroquinone are particularly preferred, and even more particularly preferred is 2-(2-chlorophenyl) hydroquinone hydrate. Suitable hydroquinones are further disclosed, for example, in U.S. Patent Application Publication No. 2007/0213440, the entire disclosure of which is hereby incorporated herein by reference.

Suitable benzoquinones include compounds represented by the following formula, and hydrates thereof:



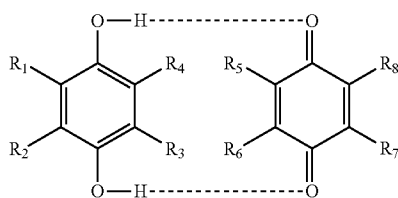
wherein each R₁, R₂, R₃, and R₄ is independently selected from the group consisting of hydrogen, a halogen group (F, Cl, Br, I), an alkyl group, a carboxyl group (—COOH) and metal salts thereof (e.g., —COO[−]M⁺) and esters thereof (—COOR), an acetate group (—CH₂COOH) and esters thereof (—CH₂COOR), a formyl group (—CHO), an acyl group (—COR), an acetyl group (—COCH₃), a halogenated carbonyl group (—COX), a sulfo group (—SO₃H) and esters thereof (—SO₃R), a halogenated sulfonyl group (—SO₂X), a sulfino group (—SO₂H), an alkylsulfinyl group (—SOR), a carbamoyl group (—CONH₂), a halogenated alkyl group, a cyano group (—CN), an alkoxy group (—OR), a hydroxy group (—OH) and metal salts thereof (e.g., —O[−]M⁺), an amino group (—NH₂), a nitro group (—NO₂), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl (—C(CH₃)₂phenyl); benzyl (—CH₂phenyl)], a nitroso group (—NO), an aceta-

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mido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). Particularly preferred benzoquinones include compounds represented by the above formula, and hydrates thereof, wherein each R_1 , R_2 , R_3 , and R_4 is independently selected from the group consisting of: a metal salt of a carboxyl group (e.g., $-\text{COO}^-\text{M}^+$), an acetate group ($-\text{CH}_2\text{COOH}$) and esters thereof ($-\text{CH}_2\text{COOR}$), a hydroxy group ($-\text{OH}$), a metal salt of a hydroxy group (e.g., $-\text{O}^-\text{M}^+$), an amino group ($-\text{NH}_2$), a nitro group ($-\text{NO}_2$), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl ($-\text{C}(\text{CH}_3)_2\text{phenyl}$); benzyl ($-\text{CH}_2\text{phenyl}$)], a nitroso group ($-\text{NO}$), an acetamido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). Methyl p-benzoquinone and tetrachloro p-benzoquinone are more particularly preferred. Suitable benzoquinones are further disclosed, for example, in U.S. Patent Application Publication No. 2007/0213442, the entire disclosure of which is hereby incorporated herein by reference.

Suitable quinhydrones include, but are not limited to, compounds represented by the following formula, and hydrates thereof:

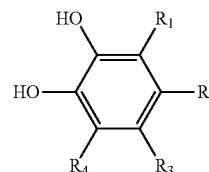


wherein each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 is independently selected from the group consisting of hydrogen, a halogen group (F, Cl, Br, I), an alkyl group, a carboxyl group ($-\text{COOH}$) and metal salts thereof (e.g., $-\text{COO}^-\text{M}^+$) and esters thereof ($-\text{COOR}$), an acetate group ($-\text{CH}_2\text{COOH}$) and esters thereof ($-\text{CH}_2\text{COOR}$), a formyl group ($-\text{CHO}$), an acyl group ($-\text{COR}$), an acetyl group ($-\text{COCH}_3$), a halogenated carbonyl group ($-\text{COX}$), a sulfo group ($-\text{SO}_3\text{H}$) and esters thereof ($-\text{SO}_3\text{R}$), a halogenated sulfonyl group ($-\text{SO}_2\text{X}$), a sulfinio group ($-\text{SO}_2\text{H}$), an alkylsulfinyl group ($-\text{SOR}$), a carbamoyl group ($-\text{CONH}_2$), a halogenated alkyl group, a cyano group ($-\text{CN}$), an alkoxy group ($-\text{OR}$), a hydroxy group ($-\text{OH}$) and metal salts thereof (e.g., $-\text{O}^-\text{M}^+$), an amino group ($-\text{NH}_2$), a nitro group ($-\text{NO}_2$), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl ($-\text{C}(\text{CH}_3)_2\text{phenyl}$); benzyl ($-\text{CH}_2\text{phenyl}$)], a nitroso group ($-\text{NO}$), an acetamido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). Particularly preferred quinhydrones include compounds represented by the above formula, and hydrates thereof, wherein each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 is independently selected from the group consisting of: a metal salt of a carboxyl group (e.g., $-\text{COO}^-\text{M}^+$), an acetate group ($-\text{CH}_2\text{COOH}$) and esters thereof ($-\text{CH}_2\text{COOR}$), a hydroxy group ($-\text{OH}$), a metal salt of a hydroxy group (e.g., $-\text{O}^-\text{M}^+$), an amino group ($-\text{NH}_2$), a nitro group ($-\text{NO}_2$), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl ($-\text{C}(\text{CH}_3)_2\text{phenyl}$); benzyl ($-\text{CH}_2\text{phenyl}$)], a nitroso group ($-\text{NO}$), an acetamido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). Particularly preferred quinhydrones also include compounds represented by the above formula wherein each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 is hydrogen. Suitable quinhydrones are further disclosed, for example, in

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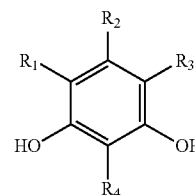
U.S. Patent Application Publication No. 2007/0213441, the entire disclosure of which is hereby incorporated herein by reference.

Suitable catechols include compounds represented by the following formula, and hydrates thereof:



wherein each R_1 , R_2 , R_3 , and R_4 , is independently selected from the group consisting of hydrogen, a halogen group (F, Cl, Br, I), an alkyl group, a carboxyl group ($-\text{COOH}$) and metal salts thereof (e.g., $-\text{COO}^-\text{M}^+$) and esters thereof ($-\text{COOR}$), an acetate group ($-\text{CH}_2\text{COOH}$) and esters thereof ($-\text{CH}_2\text{COOR}$), a formyl group ($-\text{CHO}$), an acyl group ($-\text{COR}$), an acetyl group ($-\text{COCH}_3$), a halogenated carbonyl group ($-\text{COX}$), a sulfo group ($-\text{SO}_3\text{H}$) and esters thereof ($-\text{SO}_3\text{R}$), a halogenated sulfonyl group ($-\text{SO}_2\text{X}$), a sulfinio group ($-\text{SO}_2\text{H}$), an alkylsulfinyl group ($-\text{SOR}$), a carbamoyl group ($-\text{CONH}_2$), a halogenated alkyl group, a cyano group ($-\text{CN}$), an alkoxy group ($-\text{OR}$), a hydroxy group ($-\text{OH}$) and metal salts thereof (e.g., $-\text{O}^-\text{M}^+$), an amino group ($-\text{NH}_2$), a nitro group ($-\text{NO}_2$), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl ($-\text{C}(\text{CH}_3)_2\text{phenyl}$); benzyl ($-\text{CH}_2\text{phenyl}$)], a nitroso group ($-\text{NO}$), an acetamido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). Suitable catechols are further disclosed, for example, in U.S. Patent Application Publication No. 2007/0213144, the entire disclosure of which is hereby incorporated herein by reference.

Suitable resorcinols include compounds represented by the following formula, and hydrates thereof:



wherein each R_1 , R_2 , R_3 , and R_4 , is independently selected from the group consisting of hydrogen, a halogen group (F, Cl, Br, I), an alkyl group, a carboxyl group ($-\text{COOH}$) and metal salts thereof (e.g., $-\text{COO}^-\text{M}^+$) and esters thereof ($-\text{COOR}$), an acetate group ($-\text{CH}_2\text{COOH}$) and esters thereof ($-\text{CH}_2\text{COOR}$), a formyl group ($-\text{CHO}$), an acyl group ($-\text{COR}$), an acetyl group ($-\text{COCH}_3$), a halogenated carbonyl group ($-\text{COX}$), a sulfo group ($-\text{SO}_3\text{H}$) and esters thereof ($-\text{SO}_3\text{R}$), a halogenated sulfonyl group ($-\text{SO}_2\text{X}$), a sulfinio group ($-\text{SO}_2\text{H}$), an alkylsulfinyl group ($-\text{SOR}$), a carbamoyl group ($-\text{CONH}_2$), a halogenated alkyl group, a cyano group ($-\text{CN}$), an alkoxy group ($-\text{OR}$), a hydroxy group ($-\text{OH}$) and metal salts thereof (e.g., $-\text{O}^-\text{M}^+$), an amino group ($-\text{NH}_2$), a nitro group ($-\text{NO}_2$), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy,

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etc.), an arylalkyl group [e.g., cumyl ($-\text{C}(\text{CH}_3)_2\text{phenyl}$); benzyl ($-\text{CH}_2\text{phenyl}$)], a nitroso group ($-\text{NO}$), an acetamido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). 2-Nitroresorcinol is particularly preferred. Suitable resorcinols are further disclosed, for example, in U.S. Patent Application Publication No. 2007/0213144, the entire disclosure of which is hereby incorporated herein by reference.

When the rubber composition includes one or more hydroquinones, benzoquinones, quinhydrones, catechols, resorcinols, or a combination thereof, the total amount of hydroquinone(s), benzoquinone(s), quinhydrone(s), catechol(s), and/or resorcinol(s) present in the composition is typically at least 0.1 parts by weight or at least 0.15 parts by weight or at least 0.2 parts by weight per 100 parts of the base rubber, or an amount within the range having a lower limit of 0.1 parts or 0.15 parts or 0.25 parts or 0.3 parts or 0.375 parts by weight per 100 parts of the base rubber, and an upper limit of 0.5 parts or 1 part or 1.5 parts or 2 parts or 3 parts by weight per 100 parts of the base rubber.

In a particular embodiment, the soft and fast agent is selected from zinc pentachlorothiophenol, pentachlorothiophenol, ditolyl disulfide, diphenyl disulfide, dixylyl disulfide, 2-nitroresorcinol, and combinations thereof.

Suitable types and amounts of base rubber, initiator agent, coagent, filler, and additives are more fully described in, for example, U.S. Pat. Nos. 6,566,483, 6,695,718, and 6,939,907, 7,041,721 and 7,138,460, the entire disclosures of which are hereby incorporated herein by reference.

The outer core layer is preferably formed from a highly resilient thermoplastic polymer such as a highly neutralized polymer ("HNP") composition. HNP compositions suitable for use in forming the outer core layer of golf balls of the present invention preferably have a material hardness of 35 Shore D or greater, and more preferably have a hardness of 45 Shore D or greater or a hardness within a range having a lower limit of 45 or 50 or 55 or 57 or 58 or 60 or 65 or 70 or 75 Shore D and an upper limit of 80 or 85 or 90 or 95 Shore D.

Suitable HNP compositions for use in forming the outer core layer comprise an HNP and optionally melt flow modifier(s), additive(s), and/or filler(s). Suitable HNPs are salts of acid copolymers. It is understood that the HNP may be a blend of two or more HNPs. Preferred acid copolymers are copolymers of an α -olefin and a C_3 - C_8 α,β -ethylenically unsaturated carboxylic acid. The acid is typically present in the acid copolymer in an amount within a range having a lower limit of 1 or 10 or 12 or 15 or 20 wt % and an upper limit of 25 or 30 or 35 or 40 wt %, based on the total weight of the acid copolymer. The α -olefin is preferably selected from ethylene and propylene. The acid is preferably selected from (meth) acrylic acid, ethacrylic acid, maleic acid, crotonic acid, fumaric acid, and itaconic acid. (Meth) acrylic acid is particularly preferred. Suitable acid copolymers include partially neutralized acid polymers. Examples of suitable partially neutralized acid polymers include, but are not limited to, Surlyn® ionomers, commercially available from E. I. du Pont de Nemours and Company; AClyn® ionomers, commercially available from Honeywell International Inc.; and Iotek® ionomers, commercially available from ExxonMobil Chemical Company. Also suitable are DuPont® HPF 1000 and DuPont® HPF 2000, ionomeric materials commercially available from E. I. du Pont de Nemours and Company. In a preferred embodiment, the acid polymer of the HNP outer core layer composition has a modulus within a range having a lower limit of 25,000 or 27,000 or 30,000 or 40,000 or 45,000 or 50,000 or 55,000 or 60,000 psi and an upper limit of 72,000 or 75,000 or 100,000 or 150,000 psi. As used herein,

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"modulus" refers to flexural modulus as measured using a standard flex bar according to ASTM D790-B. Additional suitable acid polymers are more fully described, for example, in U.S. Pat. Nos. 6,562,906, 6,762,246, and 6,953,820 and U.S. Patent Application Publication Nos. 2005/0049367, 2005/0020741, and 2004/0220343, the entire disclosures of which are hereby incorporated herein by reference.

The HNP is formed by reacting the acid copolymer with a sufficient amount of cation source such that at least 80%, preferably at least 90%, more preferably at least 95%, and even more preferably 100%, of all acid groups present are neutralized. Suitable cation sources include metal ions and compounds of alkali metals, alkaline earth metals, and transition metals; metal ions and compounds of rare earth elements; silicone, silane, and silicate derivatives and complex ligands; and combinations thereof. Preferred cation sources are metal ions and compounds of magnesium, sodium, potassium, cesium, calcium, barium, manganese, copper, zinc, tin, lithium, and rare earth metals. Metal ions and compounds of calcium and magnesium are particularly preferred. The acid copolymer may be at least partially neutralized prior to contacting the acid copolymer with the cation source to form the HNP. Methods of preparing ionomers, and the acid copolymers on which ionomers are based, are disclosed, for example, in U.S. Pat. Nos. 3,264,272, and 4,351,931, and U.S. Patent Application Publication No. 2002/0013413.

HNP outer core layer compositions of the present invention optionally contain one or more melt flow modifiers. The amount of melt flow modifier in the composition is readily determined such that the melt flow index of the composition is at least 0.1 g/10 min, preferably from 0.5 g/10 min to 10.0 g/10 min, and more preferably from 1.0 g/10 min to 6.0 g/10 min, as measured using ASTM D-1238, condition E, at 190° C., using a 2160 gram weight.

Suitable melt flow modifiers include, but are not limited to, high molecular weight organic acids and salts thereof, polyamides, polyesters, polyacrylates, polyurethanes, polyethers, polyureas, polyhydric alcohols, and combinations thereof. Suitable organic acids are aliphatic organic acids, aromatic organic acids, saturated mono-functional organic acids, unsaturated monofunctional organic acids, multi-unsaturated mono-functional organic acids, and dimerized derivatives thereof. Particular examples of suitable organic acids include, but are not limited to, caproic acid, caprylic acid, capric acid, lauric acid, stearic acid, behenic acid, erucic acid, oleic acid, linoleic acid, myristic acid, benzoic acid, palmitic acid, phenylacetic acid, naphthalenoic acid, dimerized derivatives thereof. Suitable organic acids are more fully described, for example, in U.S. Pat. No. 6,756,436, the entire disclosure of which is hereby incorporated herein by reference.

Additional melt flow modifiers suitable for use in compositions of the present invention, include the non-fatty acid melt flow modifiers described in U.S. Pat. Nos. 7,365,128 and 7,402,629, the entire disclosures of which are hereby incorporated herein by reference.

HNP outer core layer compositions of the present invention optionally include additive(s) and/or filler(s) in an amount within a range having a lower limit of 0 or 5 or 10 wt %, and an upper limit of 25 or 30 or 50 wt %, based on the total weight of the composition. Suitable additives and fillers include, but are not limited to, chemical blowing and foaming agents, optical brighteners, coloring agents, fluorescent agents, whitening agents, UV absorbers, light stabilizers, defoaming agents, processing aids, mica, talc, nano-fillers, antioxidants, stabilizers, softening agents, fragrance components, plasticizers, impact modifiers, TiO_2 , acid copolymer wax, surfactants, and fillers, such as zinc oxide, tin oxide, barium sulfate,

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zinc sulfate, calcium oxide, calcium carbonate, zinc carbonate, barium carbonate, clay, tungsten, tungsten carbide, silica, lead silicate, regrind (recycled material), and mixtures thereof. Suitable additives are more fully described in, for example, U.S. Patent Application Publication No. 2003/0225197, the entire disclosure of which is hereby incorporated herein by reference.

In a particular embodiment, the HNP outer core layer composition has a moisture vapor transmission rate ("MVTR") of 8 g-mil/100 in²/day or less (i.e., 3.2 g-mm/m²·day or less), or 5 g-mil/100 in²/day or less (i.e., 2.0 g-mm/m²·day or less), or 3 g-mil/100 in²/day or less (i.e., 1.2 g-mm/m²·day or less), or 2 g-mil/100 in²/day or less (i.e., 0.8 g-mm/m²·day or less), or 1 g-mil/100 in²/day or less (i.e., 0.4 g-mm/m²·day or less), or less than 1 g-mil/100 in²/day (i.e., less than 0.4 g-mm/m²·day). Suitable moisture resistant HNP compositions are disclosed, for example, in U.S. Patent Application Publication Nos. 2005/0267240, 2006/0106175 and 2006/0293464, the entire disclosures of which are hereby incorporated herein by reference.

In another particular embodiment, a sphere formed from the HNP outer core layer composition has a compression of 70 or greater, or 80 or greater, or a compression within a range having a lower limit of 70 or 80 or 90 or 100 and an upper limit of 110 or 130 or 140.

HNP outer core layer compositions of the present invention are not limited by any particular method or any particular equipment for making the compositions. In a preferred embodiment, the composition is prepared by the following process. The acid polymer(s), preferably an ethylene/(meth)acrylic acid copolymer, optional melt flow modifier(s), and optional additive(s)/filler(s) are simultaneously or individually fed into a melt extruder, such as a single or twin screw extruder. A suitable amount of cation source is then added such that at least 80%, preferably at least 90%, more preferably at least 95%, and even more preferably 100%, of all acid groups present are neutralized. The acid polymer may be at least partially neutralized prior to the above process. The components are intensively mixed prior to being extruded as a strand from the die-head.

Suitable HNP outer core layer compositions of the present invention also include blends of HNPs with partially neutralized ionomers as disclosed, for example, in U.S. Patent Application Publication No. 2006/0128904, the entire disclosure of which is hereby incorporated herein by reference, and blends of HNPs with additional thermoplastic and elastomeric materials. Examples of thermoplastic materials suitable for blending include bimodal ionomers (e.g., as disclosed in U.S. Patent Application Publication No. 2004/0220343 and U.S. Pat. Nos. 6,562,906, 6,762,246 and 7,273,903, the entire disclosures of which are hereby incorporated herein by reference), ionomers modified with rosins (e.g., as disclosed in U.S. Patent Application Publication No. 2005/0020741, the entire disclosure of which is hereby incorporated by reference), soft and resilient ethylene copolymers (e.g., as disclosed U.S. Patent Application Publication No. 2003/0114565, the entire disclosure of which is hereby incorporated herein by reference), polyolefins, polyamides, polyesters, polyethers, polycarbonates, polysulfones, polyacetals, polylactones, acrylonitrile-butadiene-styrene resins, polyphenylene oxide, polyphenylene sulfide, styrene-acrylonitrile resins, styrene maleic anhydride, polyimides, aromatic polyketones, ionomers and ionomeric precursors, acid copolymers, conventional HNPs, polyurethanes, grafted and non-grafted metallocene-catalyzed polymers, single-site catalyst polymerized polymers, high crystalline acid polymers, cationic ionomers, and combinations thereof. Particu-

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lar polyolefins suitable for blending include one or more, linear, branched, or cyclic, C₂-C₄₀ olefins, particularly polymers comprising ethylene or propylene copolymerized with one or more C₂-C₄₀ olefins, C₃-C₂₀ α-olefins, or C₃-C₁₀ α-olefins. Particular conventional HNPs suitable for blending include, but are not limited to, one or more of the HNPs disclosed in U.S. Pat. Nos. 6,756,436, 6,894,098, and 6,953,820, the entire disclosures of which are hereby incorporated herein by reference. Examples of elastomers suitable for blending include natural and synthetic rubbers, including, but not limited to, ethylene propylene rubber ("EPR"), ethylene propylene diene rubber ("EPDM"), styrenic block copolymer rubbers (such as SI, SIS, SB, SBS, SIBS, and the like, where "S" is styrene, "I" is isobutylene, and "B" is butadiene), butyl rubber, halobutyl rubber, copolymers of isobutylene and para-alkylstyrene, halogenated copolymers of isobutylene and para-alkylstyrene, natural rubber, polyisoprene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and polybutadiene rubber (cis and trans). Additional suitable blend polymers include those described in U.S. Pat. No. 5,981,658, for example at column 14, lines 30 to 56, the entire disclosure of which is hereby incorporated herein by reference. The blends described herein may be produced by post-reactor blending, by connecting reactors in series to make reactor blends, or by using more than one catalyst in the same reactor to produce multiple species of polymer. The polymers may be mixed prior to being put into an extruder, or they may be mixed in an extruder.

HNP outer core layer compositions of the present invention, in the neat (i.e., unfilled) form, preferably have a specific gravity of from 0.95 g/cc to 0.99 g/cc. Any suitable filler, flake, fiber, particle, or the like, of an organic or inorganic material may be added to the HNP composition to increase or decrease the specific gravity, particularly to adjust the weight distribution within the golf ball, as further disclosed in U.S. Pat. Nos. 6,494,795, 6,547,677, 6,743,123, 7,074,137, and 6,688,991, the entire disclosures of which are hereby incorporated herein by reference.

Suitable HNP compositions are further disclosed, for example, in U.S. Pat. Nos. 6,653,382, 6,756,436, 6,777,472, 6,894,098, 6,919,393, and 6,953,820, the entire disclosures of which are hereby incorporated herein by reference.

Particularly suitable for use in forming outer core layers of golf balls of the present invention are the "relatively hard HNP compositions" disclosed in U.S. Patent Application Publication No. 2007/0207879, the "high modulus HNP compositions" disclosed in U.S. Pat. No. 7,207,903, and the highly neutralized acid polymer compositions disclosed in U.S. Pat. No. 6,994,638, the entire disclosures of which are hereby incorporated herein by reference.

The outer core layer is alternatively formed from a highly resilient thermoplastic polymer composition selected from Hytrel® thermoplastic polyester elastomers, commercially available from E. I. du Pont de Nemours and Company, and Pebax® thermoplastic polyether block amides, commercially available from Arkema Inc.

Additional materials suitable for forming the inner and outer core layers include the core compositions disclosed in U.S. Pat. No. 7,300,364, the entire disclosure of which is hereby incorporated herein by reference. For example, suitable core materials include HNPs neutralized with organic fatty acids and salts thereof, metal cations, or a combination of both. In addition to HNPs neutralized with organic fatty acids and salts thereof, core compositions may comprise at

least one rubber material having a resilience index of at least about 40. Preferably the resilience index is at least about 50.

The weight distribution of the cores disclosed herein can be varied to achieve certain desired parameters, such as spin rate, compression, and initial velocity.

The two-layer core is enclosed with a cover comprising an inner cover layer and an outer cover layer. According to the present invention, the surface hardness of the outer core layer's outer surface is greater than the material hardness of the inner cover layer. In a particular embodiment, the surface hardness of the outer core layer's outer surface is greater than the material hardness of both the inner cover layer and the outer cover layer.

It should be understood that there is a fundamental difference between "material hardness" and "hardness as measured directly on a golf ball." For purposes of the present disclosure, material hardness is measured according to ASTM D2240 and generally involves measuring the hardness of a flat "slab" or "button" formed of the material. Hardness as measured directly on a golf ball (or other spherical surface) typically results in a different hardness value. This difference in hardness values is due to several factors including, but not limited to, ball construction (i.e., core type, number of core and/or cover layers, etc.), ball (or sphere) diameter, and the material composition of adjacent layers. It should also be understood that the two measurement techniques are not linearly related and, therefore, one hardness value cannot easily be correlated to the other. Unless otherwise stated, the material hardness values given herein for cover materials are measured according to ASTM D2240, with all values reported following 10 days of aging at 50% relative humidity and 23° C.

The inner cover layer preferably has an outer surface hardness of 95 Shore C or less, or an outer surface hardness within a range having a lower limit of 80 or 85 or 87 Shore C and an upper limit of 90 or 91 or 95 Shore C. For purposes of the present disclosure, the outer surface hardness of the inner cover layer is measured according to the procedure given herein for measuring the outer surface hardness of a golf ball layer.

The inner cover layer preferably has a material hardness ($H_{inner\ cover}$) of 95 Shore C or less, or less than 95 Shore C, or 92 Shore C or less, or 90 Shore C or less, or has a material hardness ($H_{inner\ cover}$) within a range having a lower limit of 70 or 75 or 80 or 84 or 85 or 87 Shore C and an upper limit of 90 or 91 or 92 or 95 Shore C. The thickness of the inner cover layer is preferably within a range having a lower limit of 0.010 or 0.015 or 0.020 or 0.025 or 0.030 inches and an upper limit of 0.035 or 0.045 or 0.050 or 0.080 or 0.120 or 0.150 inches.

The outer cover layer preferably has an outer surface hardness within a range having a lower limit of 20 or 30 or 35 or 40 Shore D and an upper limit of 52 or 58 or 60 or 65 or 70 or 72 or 75 Shore D.

The outer cover layer preferably has a material hardness of 85 Shore C or less. The thickness of the outer cover layer is preferably within a range having a lower limit of 0.010 or 0.015 or 0.020 or 0.025 inches and an upper limit of 0.035 or 0.040 or 0.050 or 0.055 or 0.080 inches.

Optional intermediate cover layers may be included and generally have a thickness within a range having a lower limit of 0.010 or 0.020 or 0.025 inches and an upper limit of 0.050 or 0.150 or 0.200 inches.

The cover preferably has an overall thickness within a range having a lower limit of 0.010 or 0.020 or 0.025 or 0.030 or 0.040 or 0.045 or 0.050 or 0.060 inches and an upper limit of 0.070 or 0.075 or 0.080 or 0.090 or 0.100 or 0.150 or 0.200 or 0.300 or 0.500 inches.

Cover materials are preferably cut-resistant materials, selected based on the desired performance characteristics. Suitable inner and outer cover layer materials for the golf balls disclosed herein include, but are not limited to, ionomer resins and blends thereof (e.g., Surlyn® ionomer resins and DuPont® HPF 1000 and HPF 2000, commercially available from E. I. du Pont de Nemours and Company; Iotek® ionomers, commercially available from ExxonMobil Chemical Company; Amplify® IO ionomers of ethylene acrylic acid copolymers, commercially available from The Dow Chemical Company; and Clarix® ionomer resins, commercially available from A. Schulman Inc.); polyurethanes; polyureas; copolymers and hybrids of polyurethane and polyurea; polyethylene, including, for example, low density polyethylene, linear low density polyethylene, and high density polyethylene; polypropylene; rubber-toughened olefin polymers; acid copolymers, e.g., (meth)acrylic acid, which do not become part of an ionomeric copolymer; plastomers; flexomers; styrene/butadiene/styrene block copolymers; styrene/ethylene/butylene/styrene block copolymers; dynamically vulcanized elastomers; ethylene vinyl acetates; ethylene methyl acrylates; polyvinyl chloride resins; polyamides, amide-ester elastomers, and graft copolymers of ionomer and polyamide, including, for example, Pebax® thermoplastic polyether block amides, commercially available from Arkema Inc; crosslinked trans-polyisoprene and blends thereof; polyester-based thermoplastic elastomers, such as Hytrel®, commercially available from E. I. du Pont de Nemours and Company; polyurethane-based thermoplastic elastomers, such as Elastollan®, commercially available from BASF; synthetic or natural vulcanized rubber; and combinations thereof. Suitable cover materials and constructions also include, but are not limited to, those disclosed in U.S. Pat. Nos. 6,117,025, 6,767,940, and 6,960,630, the entire disclosures of which are hereby incorporated herein by reference.

Compositions comprising an ionomer or a blend of two or more ionomers are particularly suitable for forming the inner cover layer in dual-layer covers. Preferred ionomeric compositions include:

- (a) a composition comprising a "high acid ionomer" (i.e., having an acid content of greater than 16 wt %), such as Surlyn 8150®, a copolymer of ethylene and methacrylic acid, having an acid content of 19 wt %, which is 45% neutralized with sodium;
- (b) a composition comprising a high acid ionomer and a maleic anhydride-grafted non-ionomeric polymer (e.g., Fusabond® maleic anhydride-grafted metallocene-catalyzed ethylene-butene copolymers). A particularly preferred blend of high acid ionomer and maleic anhydride-grafted polymer is a blend of 79-85 wt % Surlyn 8150® and 15-21 wt % Fusabond®. Blends of high acid ionomers with maleic anhydride-grafted polymers are further disclosed, for example, in U.S. Pat. Nos. 6,992,135 and 6,677,401, the entire disclosures of which are hereby incorporated herein by reference;
- (c) a composition comprising a 50/45/5 blend of Surlyn® 8940/Surlyn® 9650/Nucrel® 960, preferably having a material hardness of from 80 to 85 Shore C;
- (d) a composition comprising a 50/25/25 blend of Surlyn® 8940/Surlyn® 9650/Surlyn® 9910, preferably having a material hardness of about 90 Shore C;
- (e) a composition comprising a 50/50 blend of Surlyn® 8940/Surlyn® 9650, preferably having a material hardness of about 86 Shore C;
- (f) a composition comprising a blend of Surlyn® 7940/Surlyn® 8940, optionally including a melt flow modifier;

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(g) a composition comprising a blend of a first high acid ionomer and a second high acid ionomer, wherein the first high acid ionomer is neutralized with a different cation than the second high acid ionomer (e.g., 50/50 blend of Surlyn® 8150 and Surlyn® 9150), optionally including one or more melt flow modifiers such as an ionomer, ethylene-acid copolymer or ester terpolymer; and

(h) a composition comprising a blend of a first high acid ionomer and a second high acid ionomer, wherein the first high acid ionomer is neutralized with a different cation than the second high acid ionomer, and from 0 to 10 wt % of an ethylene/acid/ester ionomer wherein the ethylene/acid/ester ionomer is neutralized with the same cation as either the first high acid ionomer or the second high acid ionomer or a different cation than the first and second high acid ionomers (e.g., a blend of 40-50 wt % Surlyn® 8140, 40-50 wt % Surlyn® 9120, and 0-10 wt % Surlyn® 6320).

Surlyn 8150®, Surlyn® 8940, and Surlyn® 8140 are different grades of E/MAA copolymer in which the acid groups have been partially neutralized with sodium ions. Surlyn® 9650, Surlyn® 9910, Surlyn® 9150, and Surlyn® 9120 are different grades of E/MAA copolymer in which the acid groups have been partially neutralized with zinc ions. Surlyn® 7940 is an E/MAA copolymer in which the acid groups have been partially neutralized with lithium ions. Surlyn® 6320 is a very low modulus magnesium ionomer with a medium acid content. Nucrel® 960 is an E/MAA copolymer resin nominally made with 15 wt % methacrylic acid. Surlyn® ionomers, Fusabond® copolymers, and Nucrel® copolymers are commercially available from E. I. du Pont de Nemours and Company.

Non-limiting examples of particularly preferred ionomeric cover layer formulations are shown in Table 1 below.

TABLE 1

Cover Layer Material	Surlyn® 8150, wt %	Fusabond®, wt %	Shore C Hardness*
1	89	11	91.2
2	84	16	89.8
3	84	16	90.4
4	84	16	89.6
5	81	19	88.9
6	80	20	89.1
7	78	22	88.1
8	76	24	87.6
9	76	24	87.2
10	73	27	86.6
11	71	29	86.7
12	67	33	84.0

*Flex bars of each blend composition were formed and evaluated for hardness according to ASTM D2240 following 10 days of aging at 50% relative humidity and 23° C.

Ionomeric cover compositions can be blended with non-ionic thermoplastic resins, particularly to manipulate product properties. Examples of suitable non-ionic thermoplastic resins include, but are not limited to, polyurethane, poly-ether-ester, poly-amide-ether, polyether-urea, thermoplastic poly-ether block amides (e.g., Pebax® block copolymers, commercially available from Arkema Inc.), styrene-butadiene-styrene block copolymers, styrene(ethylene-butylene)-styrene block copolymers, polyamides, polyesters, polyolefins (e.g., polyethylene, polypropylene, ethylene-propylene copolymers, polyethylene-(meth)acrylate, polyethylene-(meth)acrylic acid, functionalized polymers with maleic anhydride grafting, Fusabond® functionalized olefins com-

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mercially available from E. I. du Pont de Nemours and Company, functionalized polymers with epoxidation, elastomers (e.g., ethylene propylene diene monomer rubber, metal-locene-catalyzed polyolefin) and ground powders of thermoset elastomers.

Suitable ionomeric cover materials are further disclosed, for example, in U.S. Pat. Nos. 6,653,382, 6,756,436, 6,894,098, 6,919,393, and 6,953,820, the entire disclosures of which are hereby incorporated by reference.

Polyurethanes, polyureas, and copolymers and blends thereof are particularly suitable for forming the outer cover layer in dual-layer covers. When used as cover layer materials, polyurethanes and polyureas can be thermoset or thermoplastic. Thermoset materials can be formed into golf ball layers by conventional casting or reaction injection molding techniques. Thermoplastic materials can be formed into golf ball layers by conventional compression or injection molding techniques.

Suitable polyurethane cover materials are further disclosed in U.S. Pat. Nos. 5,334,673, 6,506,851, 6,756,436, and 7,105,623, the entire disclosures of which are hereby incorporated herein by reference. Suitable polyurea cover materials are further disclosed in U.S. Pat. Nos. 5,484,870, 6,835,794 and 7,378,483, and U.S. Patent Application Publication No. 2008/0064527, the entire disclosures of which are hereby incorporated herein by reference. Suitable polyurethane-urea cover materials include polyurethane/polyurea blends and copolymers comprising urethane and urea segments, as disclosed in U.S. Patent Application Publication No. 2007/0117923, the entire disclosure of which is hereby incorporated herein by reference.

Golf ball cover compositions may include a flow modifier, such as, but not limited to, Nucrel® acid copolymer resins, and particularly Nucrel® 960. Nucrel® acid copolymer resins are commercially available from E. I. du Pont de Nemours and Company.

Cover compositions may also include one or more filler(s), such as the fillers given above for rubber compositions of the present invention (e.g., titanium dioxide, barium sulfate, etc.), and/or additive(s), such as coloring agents, fluorescent agents, whitening agents, antioxidants, dispersants, UV absorbers, light stabilizers, plasticizers, surfactants, compatibility agents, foaming agents, reinforcing agents, release agents, and the like.

In a particular embodiment, the cover comprises an inner cover layer formed from a composition comprising a high acid ionomer and a maleic anhydride-grafted non-ionomeric polymer and an outer cover layer formed from a polyurethane, polyurea, or copolymer or hybrid of polyurethane/polyurea. The outer cover layer material may be thermoplastic or thermoset. A particularly preferred inner cover layer composition is a 84 wt %/16 wt % blend of Surlyn 8150® and Fusabond 572D®.

Additional suitable cover materials are disclosed, for example, in U.S. Patent Application Publication No. 2005/0164810, U.S. Pat. No. 5,919,100, and PCT Publications WO00/23519 and WO00/29129, the entire disclosures of which are hereby incorporated herein by reference.

Golf balls of the present invention optionally include one or more intermediate layer(s) disposed between the core and the cover. When present, the overall thickness of the intermediate layer(s) is generally within a range having a lower limit of 0.010 or 0.050 or 0.100 inches and an upper limit of 0.300 or 0.350 or 0.400 inches. Suitable intermediate layer materials include, but are not limited to, natural rubbers, balata, gutta-percha, cis-polybutadienes, trans-polybutadienes, synthetic polyisoprene rubbers, polyoctenamers, styrene-propy-

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lene-diene rubbers, metallocene rubbers, styrene-butadiene rubbers, ethylene-propylene rubbers, chloroprene rubbers, acrylonitrile rubbers, acrylonitrile-butadiene rubbers, styrene-ethylene block copolymers, maleic anhydride or succinate modified metallocene catalyzed ethylene copolymers, polypropylene resins, ionomer resins, polyamides, polyesters, polyurethanes, polyureas, chlorinated polyethylenes, polysulfide rubbers, fluorocarbons, and combinations thereof.

A moisture vapor barrier layer is optionally employed between the core and the cover. Moisture vapor barrier layers are further disclosed, for example, in U.S. Pat. Nos. 6,632, 147, 6,932,720, 7,004,854, and 7,182,702, the entire disclosures of which are hereby incorporated herein by reference.

In addition to the material disclosed above, any of the core or cover layers may comprise one or more of the following materials: thermoplastic elastomer, thermoset elastomer, synthetic rubber, thermoplastic vulcanizate, copolymeric ionomer, terpolymeric inomer, polycarbonate, polyolefin, polyamide, copolymeric polyamide, polyesters, polyester-amides, polyether-amides, polyvinyl alcohols, acrylonitrile-butadiene-styrene copolymers, polyarylate, polyacrylate, polyphenylene ether, impact-modified polyphenylene ether, high impact polystyrene, diallyl phthalate polymer, metallocene-catalyzed polymers, styrene-acrylonitrile (SAN), olefin-modified SAN, acrylonitrile-styrene-acrylonitrile, styrene-maleic anhydride (S/MA) polymer, styrenic copolymer, functionalized styrenic copolymer, functionalized styrenic terpolymer, styrenic terpolymer, cellulose polymer, liquid crystal polymer (LCP), ethylene-propylene-diene rubber (EPDM), ethylene-vinyl acetate copolymer (EVA), ethylene propylene rubber (EPR), ethylene vinyl acetate, polyurea, and polysiloxane. Suitable polyamides for use as an additional material in compositions disclosed herein also include resins obtained by: (1) polycondensation of (a) a dicarboxylic acid, such as oxalic acid, adipic acid, sebacic acid, terephthalic acid, isophthalic acid or 1,4-cyclohexanedicarboxylic acid, with (b) a diamine, such as ethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, or decamethylenediamine, 1,4-cyclohexyldiamine or m-xylylenediamine; (2) a ring-opening polymerization of cyclic lactam, such as ϵ -caprolactam or ω -lauro lactam; (3) polycondensation of an aminocarboxylic acid, such as 6-aminocaproic acid, 9-aminononanoic acid, 11-aminoundecanoic acid or 12-aminododecanoic acid; or (4) copolymerization of a cyclic lactam with a dicarboxylic acid and a diamine. Specific examples of suitable polyamides include Nylon 6, Nylon 66, Nylon 610, Nylon 11, Nylon 12, copolymerized Nylon, Nylon MXD6, and Nylon 46.

Other preferred materials suitable for use as an additional material in golf ball compositions disclosed herein include Skypel polyester elastomers, commercially available from SK Chemicals of South Korea; Septon® diblock and triblock copolymers, commercially available from Kuraray Corporation of Kurashiki, Japan; and Kraton® diblock and triblock copolymers, commercially available from Kraton Polymers LLC of Houston, Tex.

Compositions disclosed herein can be either foamed or filled with density adjusting materials to provide desirable golf ball performance characteristics.

The present invention is not limited by any particular process for forming the golf ball layer(s). It should be understood that the layer(s) can be formed by any suitable technique, including injection molding, compression molding, casting, and reaction injection molding.

When injection molding is used, the composition is typically in a pelletized or granulated form that can be easily fed

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into the throat of an injection molding machine wherein it is melted and conveyed via a screw in a heated barrel at temperatures of from 150° F. to 600° F., preferably from 200° F. to 500° F. The molten composition is ultimately injected into a closed mold cavity, which may be cooled, at ambient or at an elevated temperature, but typically the mold is cooled to a temperature of from 50° F. to 70° F. After residing in the closed mold for a time of from 1 second to 300 seconds, preferably from 20 seconds to 120 seconds, the core and/or core plus one or more additional core or cover layers is removed from the mold and either allowed to cool at ambient or reduced temperatures or is placed in a cooling fluid such as water, ice water, dry ice in a solvent, or the like.

When compression molding is used to form a core, the composition is first formed into a preform or slug of material, typically in a cylindrical or roughly spherical shape at a weight slightly greater than the desired weight of the molded core. Prior to this step, the composition may be first extruded or otherwise melted and forced through a die after which it is cut into a cylindrical preform. The preform is then placed into a compression mold cavity and compressed at a mold temperature of from 150° F. to 400° F., preferably from 250° F. to 400° F., and more preferably from 300° F. to 400° F. When compression molding a cover layer, half-shells of the cover layer material are first formed via injection molding. A core is then enclosed within two half-shells, which is then placed into a compression mold cavity and compressed.

Reaction injection molding processes are further disclosed, for example, in U.S. Pat. Nos. 6,083,119, 7,208,562, 7,281,997, 7,282,169, 7,338,391, and U.S. Patent Application Publication No. 2006/0247073, the entire disclosures of which are hereby incorporated herein by reference.

Golf balls of the present invention typically have a coefficient of restitution ("COR") of 0.700 or greater, preferably 0.750 or greater, more preferably 0.780 or greater, and even more preferably 0.790 or greater.

COR, as used herein, is determined according to a known procedure wherein a golf ball or golf ball subassembly (e.g., a golf ball core) is fired from an air cannon at two given velocities and calculated at a velocity of 125 ft/s. Ballistic light screens are located between the air cannon and the steel plate at a fixed distance to measure ball velocity. As the ball travels toward the steel plate, it activates each light screen, and the time at each light screen is measured. This provides an incoming transit time period inversely proportional to the ball's incoming velocity. The ball impacts the steel plate and rebounds through the light screens, which again measure the time period required to transit between the light screens. This provides an outgoing transit time period inversely proportional to the ball's outgoing velocity. COR is then calculated as the ratio of the outgoing transit time period to the incoming transit time period, $COR = V_{out}/V_{in} = T_{in}/T_{out}$.

Golf balls of the present invention typically have an overall compression of 40 or greater, or a compression within a range having a lower limit of 40 or 50 or 60 or 65 or 75 or 80 or 90 and an upper limit of 95 or 100 or 105 or 110 or 115 or 120. Dual cores of the present invention preferably have an overall compression of 60 or 70 or 75 or 80 and an upper limit of 85 or 90 or 95 or 100. Inner core layers of the present invention preferably have a compression of 40 or less, or from 20 to 40, or a compression of about 35.

Compression is an important factor in golf ball design. For example, the compression of the core can affect the ball's spin rate off the driver and the feel. As disclosed in Jeff Dalton's *Compression by Any Other Name, Science and Golf IV, Proceedings of the World Scientific Congress of Golf* (Eric Thain ed., Routledge, 2002) ("J. Dalton"), several different methods

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can be used to measure compression, including Atti compression, Riehle compression, load/deflection measurements at a variety of fixed loads and offsets, and effective modulus. For purposes of the present invention, "compression" refers to Atti compression and is measured according to a known procedure, using an Atti compression test device, wherein a piston is used to compress a ball against a spring. The travel of the piston is fixed and the deflection of the spring is measured. The measurement of the deflection of the spring does not begin with its contact with the ball; rather, there is an offset of approximately the first 1.25 mm (0.05 inches) of the spring's deflection. Very low stiffness cores will not cause the spring to deflect by more than 1.25 mm and therefore have a zero compression measurement. The Atti compression tester is designed to measure objects having a diameter of 42.7 mm (1.68 inches); thus, smaller objects, such as golf ball cores, must be shimmed to a total height of 42.7 mm to obtain an accurate reading. Conversion from Atti compression to Riehle (cores), Riehle (balls), 100 kg deflection, 130-10 kg deflection or effective modulus can be carried out according to the formulas given in J. Dalton.

Golf balls of the present invention will typically have dimple coverage of 60% or greater, preferably 65% or greater, and more preferably 75% or greater.

The United States Golf Association specifications limit the minimum size of a competition golf ball to 1.680 inches. There is no specification as to the maximum diameter, and golf balls of any size can be used for recreational play. Golf balls of the present invention can have an overall diameter of any size. The preferred diameter of the present golf balls is from 1.680 inches to 1.800 inches. More preferably, the present golf balls have an overall diameter of from 1.680 inches to 1.760 inches, and even more preferably from 1.680 inches to 1.740 inches.

Golf balls of the present invention preferably have a moment of inertia ("MOI") of 70-95 g·cm², preferably 75-93 g·cm², and more preferably 76-90 g·cm². For low MOI embodiments, the golf ball preferably has an MOI of 85 g·cm² or less, or 83 g·cm² or less. For high MOI embodiment, the golf ball preferably has an MOI of 86 g·cm² or greater, or 87 g·cm² or greater. MOI is measured on a model MOI-005-104 Moment of Inertia Instrument manufactured by Inertia Dynamics of Collinsville, Conn. The instrument is connected to a PC for communication via a COMM port and is driven by MOI Instrument Software version #1.2.

When numerical lower limits and numerical upper limits are set forth herein, it is contemplated that any combination of these values may be used.

All patents, publications, test procedures, and other references cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent with this invention and for all jurisdictions in which such incorporation is permitted.

While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those of ordinary skill in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein, but rather that the claims be construed as encompassing all of the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those of ordinary skill in the art to which the invention pertains.

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What is claimed is:

1. A golf ball consisting essentially of:

an inner core layer formed from a rubber composition and having a diameter of from 1.100 inches to 1.400 inches, a center hardness (H_{center}) of 40 Shore C or greater, and an outer surface hardness of 60 Shore C or greater;

an outer core layer formed from a highly neutralized polymer composition and having an outer surface hardness ($H_{outer\ core}$) of 75 Shore C or greater;

an inner cover layer formed from a thermoplastic composition and having a material hardness ($H_{inner\ cover}$) less than the outer surface hardness of the outer core layer; and

an outer cover layer formed from a composition selected from the group consisting of polyurethanes, polyureas, and copolymers and blends thereof.

2. The golf ball of claim 1, wherein $H_{outer\ core} - H_{center} \geq 20$ Shore C units.

3. The golf ball of claim 1, wherein $H_{outer\ core} - H_{center} \geq 30$ Shore C units.

4. The golf ball of claim 1, wherein H_{center} is from 40 Shore C to 80 Shore C.

5. The golf ball of claim 1, wherein the outer surface hardness of the inner core layer is from 65 Shore C to 90 Shore C.

6. The golf ball of claim 1, wherein the outer surface hardness of the inner core layer is from 70 Shore C to 85 Shore C.

7. The golf ball of claim 1, wherein $H_{outer\ core}$ is 90 Shore C or greater.

8. The golf ball of claim 1, wherein $H_{outer\ core}$ is greater than 80 Shore C, and wherein $H_{inner\ cover}$ is from 80 Shore C to 95 Shore C.

9. The golf ball of claim 1, wherein $H_{outer\ core}$ is 85 Shore C or greater, and wherein $H_{inner\ cover}$ is from 84 Shore C to 92 Shore C.

10. The golf ball of claim 1, wherein H_{center} is from 60 Shore C to 70 Shore C, the outer surface hardness of the inner core layer is from 75 Shore C to 90 Shore C, and $H_{outer\ core}$ is greater than 85 Shore C.

11. The golf ball of claim 10, wherein $H_{inner\ cover}$ is from 80 Shore C to 95 Shore C.

12. The golf ball of claim 10, wherein $H_{outer\ core}$ is greater than 87 Shore C, and wherein $H_{inner\ cover}$ is from 87 Shore C to 91 Shore C.

13. The golf ball of claim 12, wherein $H_{outer\ core}$ is 90 Shore C or greater.

14. The golf ball of claim 1, wherein the inner core layer has a compression of 40 or less.

15. The golf ball of claim 14, wherein the core has an overall dual core compression of from 75 to 95.

16. The golf ball of claim 1, wherein the core has an overall dual core diameter of from 1.520 inches to 1.590 inches.

17. A golf ball consisting essentially of:

an inner core layer formed from a rubber composition and having a diameter of from 1.100 inches to 1.400 inches, a center hardness (H_{center}) of 50 Shore C or greater, and an outer surface hardness of 65 Shore C or greater;

an outer core layer formed from a highly neutralized polymer composition and having an outer surface hardness ($H_{outer\ core}$) of 75 Shore C or greater;

an inner cover layer formed from a thermoplastic composition and having a material hardness ($H_{inner\ cover}$) of from 80 Shore C to 95 Shore C; and

an outer cover layer formed from a composition selected from the group consisting of polyurethanes, polyureas, and copolymers and blends thereof.

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18. The golf ball of claim 17, wherein $H_{outer\ core} - H_{center} \geq 20$ Shore C units.

19. The golf ball of claim 17, wherein $H_{outer\ core} - H_{center} \geq 25$ Shore C units.

20. The golf ball of claim 17, wherein $H_{outer\ core}$ is 85 Shore C or greater, and wherein $H_{inner\ cover}$ is from 84 Shore C to 92 Shore C.

21. A golf ball comprising:

a core consisting of:

an inner core layer formed from a rubber composition and having a diameter of from 1.100 inches to 1.400 inches, a center hardness (H_{center}) of from 50 Shore C to 75 Shore C, and an outer surface hardness of from 60 Shore C to 85 Shore C; and

an outer core layer formed from a highly neutralized polymer composition and having an outer surface hardness ($H_{outer\ core}$) of from 80 Shore C to 95 Shore C; and

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a cover consisting of:

an inner cover layer formed from a thermoplastic composition and having a material hardness ($H_{inner\ cover}$) of from 80 Shore C to 95 Shore C; and

an outer cover layer formed from a composition selected from the group consisting of polyurethanes, polyureas, and copolymers and blends thereof.

22. The golf ball of claim 21, wherein $H_{outer\ core} - H_{center} \geq 20$ Shore C units.

23. The golf ball of claim 21, wherein H_{center} is from 50 Shore C to 70 Shore C, and wherein $H_{outer\ core} - H_{center} \geq 25$ Shore C units.

24. The golf ball of claim 21, wherein $H_{inner\ cover}$ is from 84 Shore C to 92 Shore C.

* * * * *

Exhibit D

US008257201B2

(12) **United States Patent**
Rajagopalan et al.(10) **Patent No.:** **US 8,257,201 B2**
(45) **Date of Patent:** ***Sep. 4, 2012**(54) **MULTI-LAYER-CORE GOLF BALL HAVING
HIGHLY-NEUTRALIZED POLYMER OUTER
CORE LAYER**(75) Inventors: **Murali Rajagopalan**, South Dartmouth,
MA (US); **Michael J. Sullivan**,
Barrington, RI (US)(73) Assignee: **Acushnet Company**, Fairhaven, MA
(US)(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

This patent is subject to a terminal dis-
claimer.(21) Appl. No.: **13/238,717**(22) Filed: **Sep. 21, 2011**(65) **Prior Publication Data**

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Related U.S. Application Data(63) Continuation of application No. 12/554,010, filed on
Sep. 4, 2009, which is a continuation of application
No. 12/238,511, filed on Sep. 26, 2008, now Pat. No.
8,025,593, which is a continuation-in-part of
application No. 12/208,631, filed on Sep. 11, 2008,
now Pat. No. 8,007,375, which is a continuation of
application No. 11/347,456, filed on Feb. 3, 2006, now
Pat. No. 7,652,086, which is a continuation-in-part of
application No. 10/959,751, filed on Oct. 6, 2004, now
Pat. No. 7,230,045, which is a continuation-in-part of
application No. 10/360,233, filed on Feb. 6, 2003, now
Pat. No. 6,939,907, which is a continuation-in-part of
application No. 10/118,719, filed on Apr. 9, 2002, now
Pat. No. 6,756,436.(60) Provisional application No. 60/301,046, filed on Jun.
26, 2001.(51) **Int. Cl.**
A63B 37/04 (2006.01)(52) **U.S. Cl.** **473/373; 473/372; 473/374**(58) **Field of Classification Search** None
See application file for complete search history.(56) **References Cited****U.S. PATENT DOCUMENTS**

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Primary Examiner — Robert Sellers(74) *Attorney, Agent, or Firm* — William B. Lacy(57) **ABSTRACT**

A golf ball including an inner core layer formed from a thermoset rubber composition and having a first surface hardness; a thermoplastic outer core layer having a second surface hardness, an inner surface hardness, and being formed from a copolymer of ethylene and an α,β -unsaturated carboxylic acid, an organic acid or salt thereof, and sufficient cation source to fully-neutralize the acid groups of the copolymer; an inner cover layer; and an outer cover layer; wherein the first surface hardness is less than the second surface hardness by at least 5 Shore C and less than the inner surface hardness by at least 5 Shore C.

12 Claims, No Drawings

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MULTI-LAYER-CORE GOLF BALL HAVING HIGHLY-NEUTRALIZED POLYMER OUTER CORE LAYER

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 12/554,010, filed Sep. 4, 2009, which is a continuation of U.S. patent application Ser. No. 12/238,511, filed Sep. 26, 2008 and now U.S. Pat. No. 8,025,593, which is a continuation-in-part of U.S. patent application Ser. No. 12/208,631, filed Sep. 11, 2008 and now U.S. Pat. No. 8,007,375, which is a continuation of U.S. patent application Ser. No. 11/347,456, filed Feb. 3, 2006 and now U.S. Pat. No. 7,652,086, which is a continuation-in-part of U.S. Pat. No. 7,230,045, filed Oct. 6, 2004 as U.S. patent application Ser. No. 10/959,751, which is a continuation-in-part of U.S. Pat. No. 6,939,907, filed Feb. 6, 2003 as U.S. patent application Ser. No. 10/360,233, which is a continuation-in-part of U.S. Pat. No. 6,756,436, filed Apr. 9, 2002 as U.S. patent application Ser. No. 10/118,719, which claims priority to U.S. Provisional Patent Application No. 60/301,046, filed Jun. 26, 2001, now abandoned, all of which are incorporated herein by reference.

FIELD OF THE INVENTION

The present invention is directed to golf ball compositions and, in particular, polymer compositions including highly-neutralized polymers and blends thereof.

BACKGROUND OF THE INVENTION

Conventional golf balls can be divided into two general classes: solid and wound. Solid golf balls include one-piece, two-piece (i.e., solid core and a cover), and multi-layer (i.e., solid core of one or more layers and/or a cover of one or more layers) golf balls. Wound golf balls typically include a solid, hollow, or fluid-filled center, surrounded by a tensioned elastomeric material, and a cover. It is also possible to surround a hollow or fluid-filled center with a plurality of solid layers. Solid balls have traditionally been considered longer and more durable than wound balls, but many solid constructions lack the "feel" provided by the wound construction.

More recently, by altering ball construction and composition, manufacturers have been able to vary a wide range of playing characteristics, such as compression, velocity, "feel," and spin, optimizing each or all for various playing abilities. In particular, a variety of core and cover layer(s) constructions, such as multi-layer balls having dual cover layers and/or dual core layers, have been investigated and now allow many non-wound balls to exhibit characteristics previously maintainable in a solid-construction golf ball. These golf ball layers are typically constructed with a number of polymeric compositions and blends, including polybutadiene rubber, polyurethanes, polyamides, and ethylene-based ionomers.

Ionomers, and in particular ethylene α,β -ethylenically unsaturated carboxylic acid copolymers or a melt processible ionomer thereof, are a preferred polymer for many golf ball layers. One problem encountered with the use of ionomers as stiff layers, however, is the unprocessability of the material as the percent of neutralization of the acid group increases. Ionomers are stiffened by increasing the amount of neutralization by a metal cation or a salt thereof. Once the percent of neutralization is greater than about 60% (depending on metal

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cation selected), the melt flow of the ionomer becomes too low and the ease of processability decreases or disappears altogether.

There is a need, therefore, for ionomer compositions that are neutralized at high percentages, but in a manner that still allows resultant polymer compositions to be processible. The present invention describes such compositions and their use in a variety of golf ball core and cover layers.

SUMMARY OF THE INVENTION

The present invention is directed to a golf ball comprising a center comprising a highly-neutralized thermoplastic copolymer of ethylene and an α,β -unsaturated carboxylic acid, the acid being 100% neutralized by a salt of an organic acid, a cation source, or a suitable base of the organic acid; a cover; and an intermediate layer disposed between the center and the cover; wherein the golf ball has a first coefficient of restitution of 0.81 or greater when measured at an incoming velocity of 125 ft/s; and a sphere resulting from a combination of the center and the intermediate layer has a compression of 60 or greater.

The cation source is typically a metal cation of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, and aluminum. Ideally, the salt of an organic acid includes an organic acid, such as aliphatic organic acids, aromatic organic acids, saturated mono- or multi-functional organic acids, unsaturated mono- or multi-functional organic acids, and multi-unsaturated mono- or multi-functional organic acids. The salt of an organic acid may include stearic acid, behenic acid, erucic acid, oleic acid, linoelic acid or dimerized derivatives thereof. The salt of an organic acid includes a cation, such as barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, and calcium.

The thermoplastic polymer comprises ionomeric copolymers and terpolymers, ionomer precursors, grafted metal-locene-catalyzed polymers, high-crystalline acid polymers and their ionomers, or cationic ionomers. Preferably, the cover is injection molded, cast, reaction injection molded, or compression molded over the core. In one embodiment, the cover comprises an inner cover layer and an outer cover layer, at least one which comprises a polyurethane material, a polyurea material, a polyurethane-urea hybrid material, or a polyurea-urethane hybrid material.

The center typically has a diameter of 1.50 inches or less and the intermediate layer has a thickness of 0.090 inches or greater, preferably between 0.090 inches and 0.180 inches. The compression can be 80 or greater. Additionally, the golf ball should concurrently have a second coefficient of restitution of 0.76 or greater when measured at an incoming velocity of 160 ft/s.

The present invention is also directed to a golf ball comprising an innermost core, a cover, and an intermediate layer disposed between the innermost core and the cover, wherein the intermediate layer comprises a highly-neutralized thermoplastic copolymer of ethylene and an α,β -unsaturated carboxylic acid, the acid being 100% neutralized by a salt of an organic acid, a cation source, or a suitable base of the organic acid, and wherein a sphere resulting from a combination of the center and the intermediate layer has a compression of 60 or greater.

The intermediate layer should have a flexural modulus of 50,000 psi or greater, preferably from 60,000 psi to 150,000 psi. In one embodiment, the center has a diameter of from 0.80 inches to 1.40 inches and a compression of 30 or less, and

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the intermediate layer has flexural modulus of 50,000 psi to 70,000 psi and a thickness of 0.110 inches or greater, and the cover comprises thermoset polymer having a hardness of from 45 Shore D to 60 Shore D and a thickness from 0.020 inches to 0.040 inches. Additionally, the golf ball should concurrently have a coefficient of restitution of 0.76 or greater when measured at an incoming velocity of 160 ft/s.

Additionally, the present invention is also directed to a golf ball comprising an innermost core, a cover, and an intermediate layer disposed between the innermost core and the cover, wherein the core comprises a highly-neutralized thermoplastic copolymer of ethylene and an α,β -unsaturated carboxylic acid, the acid being 100% neutralized by a salt of an organic acid, a cation source, or a suitable base of the organic acid, and wherein a sphere resulting from a combination of the center and the intermediate layer has a compression of 60 or greater.

Preferably, the compression is 80 or greater. In one embodiment, the golf ball has a coefficient of restitution of 0.80 or greater when measured at an incoming velocity of 125 ft/s. The core should have a diameter of 1.500 inches or less and/or an intermediate layer having a thickness of 0.090 inches or greater. Preferably, the intermediate layer thickness is between 0.090 inches and 0.180 inches. In an alternative embodiment, the core has a compression of 60 or less. The intermediate layer should have a flexural modulus of 50,000 psi or greater. Also, the cover can be injection molded, cast, reaction injection molded, or compression molded over the core.

The present invention is further directed to a golf ball including an inner core layer formed from a thermoset rubber composition and having a first surface hardness; a thermoplastic outer core layer having a second surface hardness, an inner surface hardness, and being formed from a copolymer of ethylene and an α,β -unsaturated carboxylic acid, an organic acid or salt thereof, and sufficient cation source to fully-neutralize the acid groups of the copolymer; an inner cover layer; and an outer cover layer. The first surface hardness is preferably less than the second surface hardness by at least 5 Shore C and less than the inner surface hardness by at least 5 Shore C, more preferably at least 7 Shore C, most preferably at least 9 Shore C.

The present invention is also directed to a golf ball including an inner core layer formed from a first rubber composition and having a first surface hardness; an intermediate core layer formed from a second rubber composition; a thermoplastic outer core layer having a second surface hardness, an inner surface hardness, and including a copolymer of ethylene and an α,β -unsaturated carboxylic acid, an organic acid or salt thereof, and sufficient cation source to fully-neutralize the acid groups of the copolymer; an inner cover layer; and an outer cover layer. The first surface hardness is preferably less than the second surface hardness by at least 5 Shore C and less than the inner surface hardness by at least 5 Shore C, more preferably at least 7 Shore C, most preferably at least 9 Shore C.

In one embodiment, the inner core has a diameter of 0.80 inches to 1.40 inches and a compression of 30 or less, and the outer core layer has flexural modulus of 50,000 psi to 70,000 psi and a thickness of 0.110 inches or greater, and the outer cover layer comprises castable thermoset polyurethane or polyurea having a hardness of from 45 Shore D to 60 Shore D and a thickness from 0.020 inches to 0.040 inches.

In another embodiment, a core resulting from a combination of the inner core layer, the intermediate core layer, and the thermoplastic outer core layer has a compression of 60 or greater. Preferably the core has a diameter of 1.500 inches or

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less and the outer core layer has a thickness of 0.090 inches or greater. The inner core has a first elastic modulus and the outer core layer has a second elastic modulus less than the first; the inner core has a first specific gravity and the outer core layer has a second specific gravity less than the first; the inner core has a first Bashore resilience and the outer core layer has a second Bashore resilience less than the first; or the first surface hardness is less than the second surface hardness by at least 7 Shore C and less than the inner surface hardness by at least 7 Shore C.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to highly-neutralized polymers and blends thereof ("HNP") for the use in golf equipment, preferably in ball cores, intermediate layers, and/or covers. The acid moieties of the HNP's, typically ethylene-based ionomers, are preferably neutralized greater than about 70%, more preferably greater than about 90%, and most preferably at least about 100%. The HNP's can be also be blended with a second polymer component, which, if containing an acid group, may be neutralized in a conventional manner, by the organic fatty acids of the present invention, or both. The second polymer component, which may be partially or fully neutralized, preferably comprises ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, polyamides, polycarbonates, polyesters, polyurethanes, polyureas, thermoplastic elastomers, polybutadiene rubber, balata, metallocene-catalyzed polymers (grafted and non-grafted), single-site polymers, high-crystalline acid polymers, cationic ionomers, and the like. HNP polymers typically have a material hardness of between about 20 and about 80 Shore D, and a flexural modulus of between about 3,000 psi and about 200,000 psi.

In one embodiment of the present invention the HNP's are ionomers and/or their acid precursors that are preferably neutralized, either fully or partially, with organic acid copolymers or the salts thereof. The acid copolymers are preferably α -olefin, such as ethylene, C_{3-8} α,β -ethylenically unsaturated carboxylic acid, such as acrylic and methacrylic acid, copolymers. They may optionally contain a softening monomer, such as alkyl acrylate and alkyl methacrylate, wherein the alkyl groups have from 1 to 8 carbon atoms.

The acid copolymers can be described as E/X/Y copolymers where E is ethylene, X is an α,β -ethylenically unsaturated carboxylic acid, and Y is a softening comonomer. In a preferred embodiment, X is acrylic or methacrylic acid and Y is a C_{1-8} alkyl acrylate or methacrylate ester. X is preferably present in an amount from about 1 to about 35 weight percent of the polymer, more preferably from about 5 to about 30 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer. Y is preferably present in an amount from about 0 to about 50 weight percent of the polymer, more preferably from about 5 to about 25 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer.

Specific acid-containing ethylene copolymers include, but are not limited to, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl acrylate,

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ethylene/methacrylic acid/methyl acrylate, ethylene/acrylic acid/ethyl acrylate, ethylene/methacrylic acid/ethyl acrylate, and ethylene/acrylic acid/methyl acrylate copolymers. The most preferred acid-containing ethylene copolymers are, ethylene/(meth) acrylic acid/n-butyl, acrylate, ethylene/(meth) acrylic acid/ethyl acrylate, and ethylene/(meth) acrylic acid/methyl acrylate copolymers.

Ionomers are typically neutralized with a metal cation, such as Li, Na, Mg, or Zn. It has been found that by adding sufficient organic acid or salt of organic acid, along with a suitable base, to the acid copolymer or ionomer, the ionomer can be neutralized without losing processability to a level much greater than for a metal cation alone. Preferably, the acid moieties are neutralized greater than about 80%, preferably from 90-100%, most preferably 100% without losing processability. This accomplished by melt-blending an ethylene α,β -ethylenically unsaturated carboxylic acid copolymer, for example, with an organic acid or a salt of organic acid, and adding a sufficient amount of a cation source to increase the level of neutralization of all the acid moieties (including those in the acid copolymer and in the organic acid) to greater than 90%, (preferably greater than 100%).

The organic acids of the present invention are aliphatic, mono- or multi-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. The salts of organic acids of the present invention include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, salts of fatty acids, particularly stearic, bebenic, erucic, oleic, linoelic or dimerized derivatives thereof. It is preferred that the organic acids and salts of the present invention be relatively non-migratory (they do not bloom to the surface of the polymer under ambient temperatures) and non-volatile (they do not volatilize at temperatures required for melt-blending).

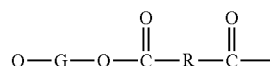
The ionomers of the invention may also be partially neutralized with metal cations. The acid moiety in the acid copolymer is neutralized about 1 to about 100%, preferably at least about 40 to about 100%, and more preferably at least about 90 to about 100%, to form an ionomer by a cation such as lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum, or a mixture thereof.

The acid copolymers of the present invention are prepared from 'direct' acid copolymers, copolymers polymerized by adding all monomers simultaneously, or by grafting of at least one acid-containing monomer onto an existing polymer. Other suitable highly-neutralized acid polymer compositions are disclosed in U.S. Patent Publication Nos. 2003/0114565 and 2005/0267240, and in U.S. patent application Ser. No. 11/270,066, which are incorporated herein, in their entirety, by reference.

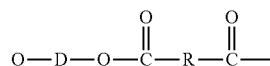
Thermoplastic polymer components, such as copolyetheresters, copolyesteresters, copolyetheramides, elastomeric polyolefins, styrene diene block copolymers and their hydrogenated derivatives, copolyesteramides, thermoplastic polyurethanes, such as copolyetherurethanes, copolyesterurethanes, copolyureaurethanes, epoxy-based polyurethanes, polycaprolactone-based polyurethanes, polyureas, and polycarbonate-based polyurethanes fillers, and other ingredients, if included, can be blended in either before, during, or after the acid moieties are neutralized, thermoplastic polyurethanes.

The copolyetheresters are comprised of a multiplicity of recurring long chain units and short chain units joined head-to-tail through ester linkages, the long chain units being represented by the formula:

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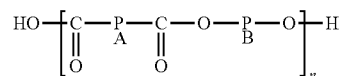


and the short chain units being represented by the formula:



where G is a divalent radical remaining after the removal of terminal hydroxyl groups from a poly(alkylene oxide)glycol having a molecular weight of about 400-8000 and a carbon to oxygen ratio of about 2.0-4.3; R is a divalent radical remaining after removal of hydroxyl groups from a diol having a molecular weight less than about 250; provided said short chain ester units amount to about 15-95 percent by weight of said copolyetherester. The preferred copolyetherester polymers are those where the polyether segment is obtained by polymerization of tetrahydrofuran and the polyester segment is obtained by polymerization of tetramethylene glycol and phthalic acid. For purposes of the invention, the molar ether: ester ratio can vary from 90:10 to 10:80; preferably 80:20 to 60:40; and the Shore D hardness is less than 70; preferably less than about 40.

The copolyetheramides are comprised of a linear and regular chain of rigid polyamide segments and flexible polyether segments, as represented by the general formula:



wherein PA is a linear saturated aliphatic polyamide sequence formed from a lactam or amino acid having a hydrocarbon chain containing 4 to 14 carbon atoms or from an aliphatic $\text{C}_6\text{-C}_8$ diamine, in the presence of a chain-limiting aliphatic carboxylic diacid having 4-20 carbon atoms; said polyamide having an average molecular weight between 300 and 15,000; and PB is a polyoxyalkylene sequence formed from linear or branched aliphatic polyoxyalkylene glycols, mixtures thereof or copolyethers derived therefrom, said polyoxyalkylene glycols having a molecular weight of less than or equal to 6000; and n indicates a sufficient number of repeating units so that said polyetheramide copolymer has an intrinsic viscosity of from about 0.6 to about 2.05. The preparation of these polyetheramides comprises the step of reacting a dicarboxylic polyamide, the COOH groups of which are located at the chain ends, with a polyoxyalkylene glycol hydroxylated at the chain ends, in the presence of a catalyst such as a tetraalkyl ortho titanate having the general formula $\text{Ti}(\text{OR})_x$ wherein R is a linear branched aliphatic hydrocarbon radical having 1 to 24 carbon atoms. Again, the more polyether units incorporated into the copolyetheramide, the softer the polymer. The ether:amide ratios are as described above for the ether:ester ratios, as is the Shore D hardness.

The elastomeric polyolefins are polymers composed of ethylene and higher primary olefins such as propylene, hexene, octene, and optionally 1,4-hexadiene and or ethylidene norbornene or norbornadiene. The elastomeric polyolefins can be optionally functionalized with maleic anhydride, epoxy, hydroxy, amine, carboxylic acid, sulfonic acid, or thiol groups.

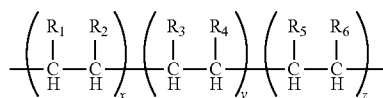
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Thermoplastic polyurethanes are linear or slightly chain branched polymers consisting of hard blocks and soft elastomeric blocks. They are produced by reacting soft hydroxy terminated elastomeric polyethers or polyesters with diisocyanates, such as methylene diisocyanate ("MDI"), p-phenylene diisocyanate ("PPDI"), or toluene diisocyanate ("TDI"). These polymers can be chain extended with glycols, secondary diamines, diacids, or amino alcohols. The reaction products of the isocyanates and the alcohols are called urethanes and these blocks are relatively hard and high melting. These hard high melting blocks are responsible for the thermoplastic nature of the polyurethanes.

Block styrene diene copolymers and their hydrogenated derivatives are composed of polystyrene units and polydiene units. They may also be functionalized with moieties such as OH, NH₂, epoxy, COOH, and anhydride groups. The polydiene units are derived from polybutadiene, polyisoprene units or copolymers of these two. In the case of the copolymer it is possible to hydrogenate the polyolefin to give a saturated rubbery backbone segments. These materials are usually referred to as SBS, SIS, or SEBS thermoplastic elastomers and they can also be functionalized with maleic anhydride.

Grafted metallocene-catalyzed polymers are also useful for blending with the HNP's of the present invention. The grafted metallocene-catalyzed polymers, while conventionally neutralized with metal cations, may also be neutralized, either partially for fully, with organic acids or salts thereof and an appropriate base. Grafted metallocene-catalyzed polymers useful, such as those disclosed in U.S. Pat. Nos. 5,703,166; 5,824,746; 5,981,658; and 6,025,442, which are incorporated herein by reference, in the golf balls of the invention are available in experimental quantities from DuPont under the tradenames SURLYN® NMO 525D, SURLYN® NMO 524D, and SURLYN® NMO 499D, all formerly known as the FUSABOND® family of polymers, or may be obtained by subjecting a non-grafted metallocene-catalyzed polymer to a post-polymerization reaction to provide a grafted metallocene-catalyzed polymer with the desired pendant group or groups. Examples of metallocene-catalyzed polymers to which functional groups may be grafted for use in the invention include, but are not limited to, homopolymers of ethylene and copolymers of ethylene and a second olefin, preferably, propylene, butene, pentene, hexene, heptene, octene, and norbornene. Generally, the invention includes golf balls having at least one layer comprising at least one grafted metallocene-catalyzed polymer or polymer blend, where the grafted metallocene-catalyzed polymer is produced by grafting a functional group onto a metallocene-catalyzed polymer having the formula:



wherein R₁ is hydrogen, branched or straight chain alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl, carbocyclic, or aromatic; R₂ is hydrogen, lower alkyl including C₁-C₅, carbocyclic, or aromatic; R₃ is hydrogen, lower alkyl including C₁-C₅, carbocyclic, or aromatic; R₄ is selected from the group consisting of H, C_nH_{2n+1}, where n=1 to 18, and phenyl, in which from 0 to 5 H within R₄ can be replaced by substituents COOH, SO₃H, NH₂, F, Cl, Br, I, OH, SH, silicone, lower alkyl esters and lower alkyl ethers, with the proviso that R₃ and R₄ can be combined to form a bicyclic

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ring; R₅ is hydrogen, lower alkyl including C₁-C₅, carbocyclic, or aromatic; R₆ is hydrogen, lower alkyl including C₁-C₅, carbocyclic, or aromatic; and wherein x, y and z are the relative percentages of each co-monomer. X can range from about 1 to 99 percent or more preferably from about 10 to about 70 percent and most preferred, from about 10 to 50 percent. Y can be from 99 to 1 percent, preferably, from 90 to 30 percent, or most preferably, 90 to 50 percent. Z can range from about 0 to about 49 percent. One of ordinary skill in the art would understand that if an acid moiety is present as a ligand in the above polymer that it may be neutralized up to 100% with an organic fatty acid as described above.

Metallocene-catalyzed copolymers or terpolymers can be random or block and may be isotactic, syndiotactic, or atactic. The pendant groups creating the isotactic, syndiotactic, or atactic polymers are chosen to determine the interactions between the different polymer chains making up the resin to control the final properties of the resins used in golf ball covers, centers, or intermediate layers. As will be clear to those skilled in the art, grafted metallocene-catalyzed polymers useful in the invention that are formed from metallocene-catalyzed random or block copolymers or terpolymers will also be random or block copolymers or terpolymers, and will have the same tacticity of the metallocene-catalyzed polymer backbone.

As used herein, the term "phrase branched or straight chain alkyl" means any substituted or unsubstituted acyclic carbon-containing compounds. Examples of alkyl groups include lower alkyl, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl or t-butyl; upper alkyl, for example, octyl, nonyl, decyl, and the like; and lower alkylene, for example, ethylene, propylene, butylene, pentene, hexene, octene, norbornene, nonene, decene, and the like.

In addition, such alkyl groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Functional groups include, but are not limited to hydroxyl, amino, carboxyl, sulfonic amide, ester, ether, phosphates, thiol, nitro, silane and halogen (fluorine, chlorine, bromine and iodine), to mention but a few.

As used herein, the term "substituted and unsubstituted carbocyclic" means cyclic carbon-containing compounds, including, but not limited to cyclopentyl, cyclohexyl, cycloheptyl, and the like. Such cyclic groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups having from 1-28 carbon atoms. The cyclic groups of the invention may further comprise a heteroatom.

As mentioned above, R₁ and R₂ can also represent any combination of alkyl, carbocyclic or aryl groups, for example, 1-cyclohexylpropyl, benzyl cyclohexylmethyl, 2-cyclohexylpropyl, 2,2-methylcyclohexylpropyl, 2,2-methylphenylpropyl, and 2,2-methylphenylbutyl.

Non-grafted metallocene-catalyzed polymers useful in the present invention are commercially available under the trade name AFFINITY® polyolefin plastomers and ENGAGE® polyolefin elastomers commercially available from Dow Chemical Company and DuPont-Dow. Other commercially available metallocene-catalyzed polymers can be used, such as EXACT®, commercially available from Exxon and INSIGHT®, commercially available from Dow. The EXACT® and INSIGHT® line of polymers also have novel rheological behavior in addition to their other properties as a result of using a metallocene catalyst technology. Metallocene-catalyzed polymers are also readily available from

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Sentinel Products Corporation of Hyannis, Mass., as foamed sheets for compression molding.

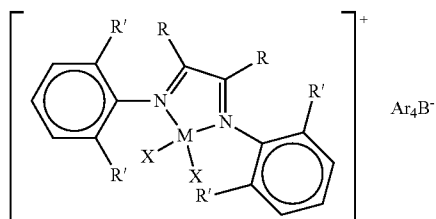
Monomers useful in the present invention include, but are not limited to, olefinic monomers having, as a functional group, sulfonic acid, sulfonic acid derivatives, such as chlorosulfonic acid, vinyl ethers, vinyl esters, primary, secondary, and tertiary amines, mono-carboxylic acids, dicarboxylic acids, partially or fully ester-derivatized mono-carboxylic and dicarboxylic acids, anhydrides of dicarboxylic acids, and cyclic imides of dicarboxylic acids.

In addition, metallocene-catalyzed polymers may also be functionalized by sulfonation, carboxylation, or the addition of an amine or hydroxy group. Metallocene-catalyzed polymers functionalized by sulfonation, carboxylation, or the addition of a hydroxy group may be converted to anionic ionomers by treatment with a base. Similarly, metallocene-catalyzed polymers functionalized by the addition of an amine may be converted to cationic ionomers by treatment with an alkyl halide, acid, or acid derivative.

The most preferred monomer is maleic anhydride, which, once attached to the metallocene-catalyzed polymer by the post-polymerization reaction, may be further subjected to a reaction to form a grafted metallocene-catalyzed polymer containing other pendant or functional groups. For example, reaction with water will convert the anhydride to a dicarboxylic acid; reaction with ammonia, alkyl, or aromatic amine forms an amide; reaction with an alcohol results in the formation of an ester; and reaction with base results in the formation of an anionic ionomer.

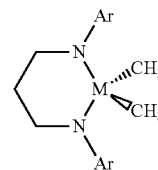
The HNP's of the present invention may also be blended with single-site and metallocene catalysts and polymers formed therefrom. As used herein, the term "single-site catalyst," such as those disclosed in U.S. Pat. No. 6,150,462 which is incorporated herein by reference, refers to a catalyst that contains an ancillary ligand that influences the steric and electronic characteristics of the polymerizing site in a manner that prevents formation of secondary polymerizing species. The term "metallocene catalyst" refers to a single-site catalyst wherein the ancillary ligands are comprising substituted or unsubstituted cyclopentadienyl groups, and the term "non-metallocene catalyst" refers to a single-site catalyst other than a metallocene catalyst.

Non-metallocene single-site catalysts include, but are not limited to, the Brookhart catalyst, which has the following structure:

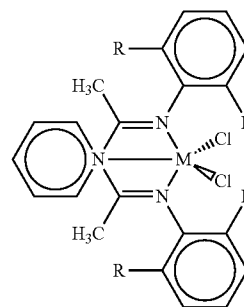


wherein M is nickel or palladium; R and R' are independently hydrogen, hydrocarbyl, or substituted hydrocarbyl; Ar is (CF₃)₂C₆H₃, and X is alkyl, methyl, hydride, or halide; the McConville catalyst, which has the structure:

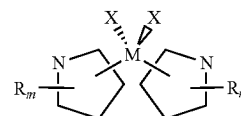
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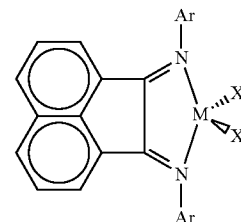
wherein M is titanium or zirconium. Iron (II) and cobalt (II) complexes with 2,6-bis(imino) pyridyl ligands, which have the structure:



where M is the metal, and R is hydrogen, alkyl, or hydrocarbyl. Titanium or zirconium complexes with pyrroles as ligands also serve as single-site catalysts. These complexes have the structure:



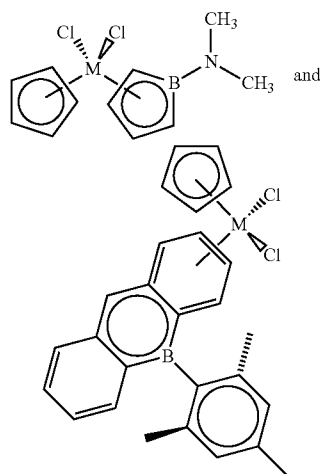
where M is the metal atom; m and n are independently 1 to 4, and indicate the number of substituent groups attached to the aromatic rings; R_m and R_n are independently hydrogen or alkyl; and X is halide or alkyl. Other examples include diimide complexes of nickel and palladium, which have the structure:



where Ar is aromatic, M is the metal, and X is halide or alkyl. Boratabenzene complexes of the Group IV or V metals also function as single-site catalysts. These complexes have the structure:

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where B is boron and M is the metal atom.

As used herein, the term “single-site catalyzed polymer” refers to any polymer, copolymer, or terpolymer, and, in particular, any polyolefin polymerized using a single-site catalyst. The term “non-metallocene single-site catalyzed polymer” refers to any polymer, copolymer, or terpolymer, and, in particular, any polyolefin polymerized using a single-site catalyst other than a metallocene-catalyst. The catalysts discussed above are examples of non-metallocene single-site catalysts. The term “metallocene catalyzed polymer” refers to any polymer, copolymer, or terpolymer, and, in particular, any polyolefin, polymerized using a metallocene catalyst.

As used herein, the term “single-site catalyzed polymer blend” refers to any blend of a single-site catalyzed polymer and any other type of polymer, preferably an ionomer, as well as any blend of a single-site catalyzed polymer with another single-site catalyzed polymer, including, but not limited to, a metallocene-catalyzed polymer.

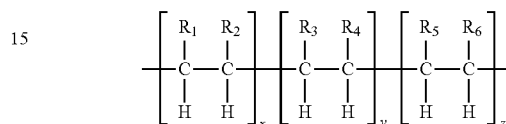
The terms “grafted single-site catalyzed polymer” and “grafted single-site catalyzed polymer blend” refer to any single-site catalyzed polymer or single-site catalyzed polymer blend in which the single-site catalyzed polymer has been subjected to a post-polymerization reaction to graft at least one functional group onto the single-site catalyzed polymer. A “post-polymerization reaction” is any reaction that occurs after the formation of the polymer by a polymerization reaction.

The single-site catalyzed polymer, which may be grafted, may also be blended with polymers, such as non-grafted single-site catalyzed polymers, grafted single-site catalyzed polymers, ionomers, and thermoplastic elastomers. Preferably, the single-site catalyzed polymer is blended with at least one ionomer of the present invention.

Grafted single-site catalyzed polymers useful in the golf balls of the invention may be obtained by subjecting a non-grafted single-site catalyzed polymer to a post-polymerization reaction to provide a grafted single-site catalyzed polymer with the desired pendant group or groups. Examples of single-site catalyzed polymers to which functional groups may be grafted for use in the invention include, but are not limited to, homopolymers of ethylene and propylene and copolymers of ethylene and a second olefin, preferably, propylene, butene, pentene, hexene, heptene, octene, and norbornene. Monomers useful in the present invention include, but are not limited to olefinic monomers having as a functional group sulfonic acid, sulfonic acid derivatives, such as

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chlorosulfonic acid, vinyl ethers, vinyl esters, primary, secondary, and tertiary amines, epoxies, isocyanates, mono-carboxylic acids, dicarboxylic acids, partially or fully ester derivatized mono-carboxylic and dicarboxylic acids, anhydrides of dicarboxylic acids, and cyclic imides of dicarboxylic acids. Generally, this embodiment of the invention includes golf balls having at least one layer comprising at least one grafted single-site catalyzed polymer or polymer blend, where the grafted single-site catalyzed polymer is produced by grafting a functional group onto a single-site catalyzed polymer having the formula:



where R₁ is hydrogen, branched or straight chain alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl, carbocyclic, aromatic or heterocyclic; R₂, R₃, R₅, and R₆ are hydrogen, lower alkyl including C₁-C₅, carbocyclic, aromatic or heterocyclic; R₄ is H, C_nH_{2n+1}, where n=1 to 18, and phenyl, in which from 0 to 5 H within R₄ can be replaced by substituents such as COOH, SO₃H, NH₂, F, Cl, Br, I, OH, SH, epoxy, isocyanate, silicone, lower alkyl esters and lower alkyl ethers; also, R₃ and R₄ can be combined to form a bicyclic ring; and x, y and z are the relative percentages of each co-monomer. X can range from about 1 to about 100 percent or more preferably from 1 to 70 percent and most preferred, from about 1 to about 50 percent. Y can be from about 99 to about 0 percent, preferably, from about 9 to about 30 percent, or most preferably, about 9 to about 50 percent. Z can range from about 0 to about 50 percent. One of ordinary skill in the art would also understand that if an acid group is selected as a ligand in the above structure that it too could be neutralized with the organic fatty acids described above.

The HNP's of the present invention may also be blended with high crystalline acid copolymers and their ionomer derivatives (which may be neutralized with conventional metal cations or the organic fatty acids and salts thereof) or a blend of a high crystalline acid copolymer and its ionomer derivatives and at least one additional material, preferably an acid copolymer and its ionomer derivatives. As used herein, the term “high crystalline acid copolymer” is defined as a “product-by-process” in which an acid copolymer or its ionomer derivatives formed from a ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to 200° C., at pressures greater than about 20,000 psi preferably greater than about 25,000 psi, more pref. from about 25,000 psi to about 50,000 psi, wherein up to about 70 percent, preferably 100 percent, of the acid groups are neutralized with a metal ion, organic fatty acids and salts thereof, or a mixture thereof. The copolymer can have a melt index (“MI”) of from about 20 to about 300 g/10 min, preferably about 20 to about 200 g/10 min, and upon neutralization of the copolymer, the resulting acid copolymer and its ionomer derivatives should have an MI of from about 0.1 to about 30.0 g/10 min.

Suitable high crystalline acid copolymer and its ionomer derivatives compositions and methods for making them are disclosed in U.S. Pat. No. 5,580,927, the disclosure of which is hereby incorporated by reference in its entirety.

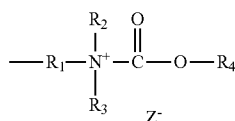
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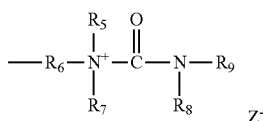
The high crystalline acid copolymer or its ionomer derivatives employed in the present invention are preferably formed from a copolymer containing about 5 to about 35 percent, more preferably from about 9 to about 18, most preferably about 10 to about 13 percent, by weight of acrylic acid, wherein up to about 75 percent, most preferably about 60 percent, of the acid groups are neutralized with an organic fatty acid, salt thereof, or a metal ion, such as sodium, lithium, magnesium, or zinc ion.

Generally speaking, high crystalline acid copolymer and its ionomer derivatives are formed by polymerization of their base copolymers at lower temperatures, but at equivalent pressures to those used for forming a conventional acid copolymer and its ionomer derivatives. Conventional acid copolymers are typically polymerized at a polymerization temperature of from at least about 200° C. to about 270° C., preferably about 220° C., and at pressures of from about 23,000 to about 30,000 psi. In comparison, the high crystalline acid copolymer and its ionomer derivatives employed in the present invention are produced from acid copolymers that are polymerized at a polymerization temperature of less than 200° C., and preferably from about 130° C. to about 200° C., and at pressures from about 20,000 to about 50,000 psi.

The HNP's of the present invention may also be blended with cationic ionomers, such as those disclosed in U.S. Pat. No. 6,193,619 which is incorporated herein by reference. In particular, cationic ionomers have a structure according to the formula:



or the formula:



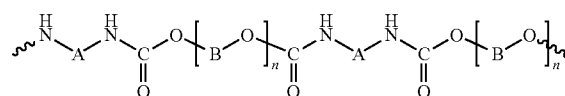
wherein R₁-R₉ are organic moieties of linear or branched chain alkyl, carbocyclic, or aryl; and Z is the negatively charged conjugate ion produced following alkylation and/or quaternization. The cationic polymers may also be quaternized up to 100% by the organic fatty acids described above.

In addition, such alkyl group may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Functional groups include but are not limited to hydroxyl, amino, carboxyl, amide, ester, ether, sulfonic, siloxane, siloxyl, silanes, sulfonyl, and halogen.

As used herein, substituted and unsubstituted carbocyclic groups of up to about 20 carbon atoms means cyclic carbon-containing compounds, including but not limited to cyclopentyl, cyclohexyl, cycloheptyl, and the like. Such cyclic groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups as described above. The cyclic groups of the invention may further comprise a heteroatom.

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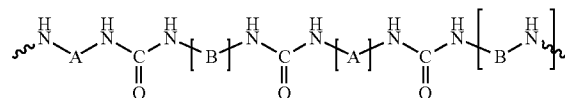
The HNP's of the present invention may also be blended with polyurethane and polyurea ionomers which include anionic moieties or groups, such as those disclosed in U.S. Pat. No. 6,207,784 which is incorporated herein by reference. Typically, such groups are incorporated onto the diisocyanate or diisocyanate component of the polyurethane or polyurea ionomers. The anionic group can also be attached to the polyol or amine component of the polyurethane or polyurea, respectively. Preferably, the anionic group is based on a sulfonic, carboxylic or phosphoric acid group. Also, more than one type of anionic group can be incorporated into the polyurethane or polyurea. Examples of anionic polyurethane ionomers with anionic groups attached to the diisocyanate moiety can have a chemical structure according to the following formula:



where A=R-Z⁻M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻ or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIIA, VIIB, VIIIB or VIIIIB metal; x=1 to 5; B is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; and n=1 to 100. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x} or Hf^{+x}.

Exemplary anionic polyurethane ionomers with anionic groups attached to the polyol component of the polyurethane are characterized by the above chemical structure where A is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; B=R-Z⁻M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻ or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIIA, VIIB, VIIIB or VIIIIB metal; x=1 to 5; and n=1 to 100. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x} or Hf^{+x}.

Examples of suitable anionic polyurea ionomers with anionic groups attached to the diisocyanate component have a chemical structure according to the following chemical structure:



where A=R-Z⁻M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻ or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIIA, VIIB, VIIIB or VIIIIB metal; x=1 to 5; and B is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x}, or Hf^{+x}.

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Suitable anionic polyurea ionomers with anionic groups attached to the amine component of the polyurea are characterized by the above chemical structure where A is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; B=R—Z—M^{+x}; R is a straight chain or branched aliphatic group, a substituted straight chain or branched aliphatic group, or an aromatic or substituted aromatic group; Z=SO₃⁻, CO₂⁻, or HPO₃⁻; M is a group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIIA, VIIB, VIIIB or VIIIB metal; and x=1 to 5. Preferably, M^{+x} is one of the following: Li⁺, Na⁺, K⁺, Mg⁺², Zn⁺², Ca⁺², Mn⁺², Al⁺³, Ti^{+x}, Zr^{+x}, W^{+x}, or Hf^{+x}. The anionic polyurethane and polyurea ionomers may also be neutralized up to 100% by the organic fatty acids described above.

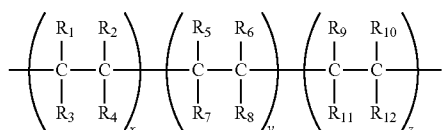
The anionic polymers useful in the present invention, such as those disclosed in U.S. Pat. No. 6,221,960 which is incorporated herein by reference, include any homopolymer, copolymer or terpolymer having neutralizable hydroxyl and/or dealkylable ether groups, and in which at least a portion of the neutralizable or dealkylable groups are neutralized or dealkylated with a metal ion.

As used herein "neutralizable" or "dealkylable" groups refer to a hydroxyl or ether group pendent from the polymer chain and capable of being neutralized or dealkylated by a metal ion, preferably a metal ion base. These neutralized polymers have improved properties critical to golf ball performance, such as resiliency, impact strength and toughness and abrasion resistance. Suitable metal bases are ionic compounds comprising a metal cation and a basic anion. Examples of such bases include hydroxides, carbonates, acetates, oxides, sulfides, and the like.

The particular base to be used depends upon the nature of the hydroxyl or ether compound to be neutralized or dealkylated, and is readily determined by one skilled in the art. Preferred anionic bases include hydroxides, carbonates, oxides and acetates.

The metal ion can be any metal ion which forms an ionic compound with the anionic base. The metal is not particularly limited, and includes alkali metals, preferably lithium, sodium or potassium; alkaline earth metals, preferably magnesium or calcium; transition metals, preferably titanium, zirconium, or zinc; and Group III and IV metals. The metal ion can have a +1 to +5 charge. Most preferably, the metal is lithium, sodium, potassium, zinc, magnesium, titanium, tungsten, or calcium, and the base is hydroxide, carbonate or acetate.

The anionic polymers useful in the present invention include those which contain neutralizable hydroxyl and/or dealkylable ether groups. Exemplary polymers include ethylene vinyl alcohol copolymers, polyvinyl alcohol, polyvinyl acetate, poly(p-hydroxymethylene styrene), and p-methoxy styrene, to name but a few. It will be apparent to one skilled in the art that many such polymers exist and thus can be used in the compositions of the invention. In general, the anionic polymer can be described by the chemical structure:



where R₁ is OH, OC(O)R_a, O-M^{+V}, (CH₂)_nR_b, (CHR_c)_nR_b, or aryl, wherein n is at least 1, R_a is a lower alkyl, M is a metal

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ion, V is an integer from 1 to 5, R_b is OH, OC(O)R_a, O-M^{+V}, and R_c is a lower alkyl or aryl, and R₂, R₃ and R₄ are each independently hydrogen, straight-chain or branched-chain lower alkyl. R₂, R₃ and R₄ may also be similarly substituted. Preferably n is from 1 to 12, more preferably 1 to 4.

The "substituted," as used herein, means one or more hydrogen atoms has been replaced by a functional group. Functional groups include, but are not limited to, hydroxyl, amino, carboxyl, sulfonic, amide, ether, ether, phosphates, thiol, nitro, silane, and halogen, as well as many others which are quite familiar to those of ordinary skill in this art.

The terms "alkyl" or "lower alkyl," as used herein, includes a group of from about 1 to 30 carbon atoms, preferably 1 to 10 carbon atoms.

In the anionic polymers useful in the present invention, at least a portion of the neutralizable or dealkylable groups of R₁ are neutralized or dealkylated by an organic fatty acid, a salt thereof, a metal base, or a mixture thereof to form the corresponding anionic moiety. The portion of the neutralizable or dealkylable groups which are neutralized or dealkylated can be between about 1 to about 100 weight percent, preferably between about 50 to about 100 weight percent, more preferably before about 90 to about 100.

Neutralization or dealkylation may be performed by melting the polymer first, then adding a metal ion in an extruder. The degree of neutralization or dealkylation is controlled by varying the amount of metal ion added. Any method of neutralization or dealkylation available to those of ordinary skill in the art may also be suitably employed.

In one embodiment, the anionic polymer is repeating units any one of the three homopolymer units in the chemical structure above. In a preferred embodiment, R₂, R₃ and R₄ are hydrogen, and R₁ is hydroxyl, i.e., the anionic polymer is a polyvinyl alcohol homopolymer in which a portion of the hydroxyl groups have been neutralized with a metal base. In another preferred embodiment, R₂, R₃ and R₄ are hydrogen, R₁ is OC(O)R_a, and R_a is methyl, i.e., the anionic polymer is a polyvinyl acetate homopolymer in which a portion of the methyl ether groups have been dealkylated with a metal ion.

The anionic polymer can also be a copolymer of two different repeating units having different substituents, or a terpolymer of three different repeating units described in the above formula. In this embodiment, the polymer can be a random copolymer, an alternating copolymer, or a block copolymer, where the term "copolymer" includes terpolymers.

In another embodiment, the anionic polymer is a copolymer, wherein R₅, R₆, R₇ and R₈ are each independently selected from the group defined above for R₂. The first unit of the copolymer can comprise from about 1 to 99 percent weight percent of the polymer, preferably from about 5 to 50 weight percent, and the second unit of the copolymer can comprise from about 99 to 1 weight percent, preferably from about 95 to 50 weight percent. In one preferred embodiment, the anionic polymer is a random, alternating or block copolymer of units (Ia) and (Ib) wherein R₁ is hydroxyl, and each of the remaining R groups is hydrogen, i.e., the polymer is a copolymer of ethylene and vinyl alcohol. In another preferred embodiment, the anionic polymer is a random, alternating or block copolymer of units (Ia) and (Ib) wherein R₁ is OC(O)R₅, where R₅ is methyl, and each of the remaining R groups is hydrogen, i.e., the polymer is a copolymer of ethylene and vinyl acetate.

In another embodiment, the anionic polymer is an anionic polymer having neutralizable hydroxyl and/or dealkylable ether groups of as in the above chemical structure wherein R₁₋₉ and R_b and R_c are as defined above; R₁₀₋₁₁ are each

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independently selected from the group as defined above for R_2 ; and R_{12} is OH or $OC(O)R_{13}$, where R_{13} is a lower alkyl; wherein x, y and z indicate relative weight percent of the different units. X can be from about 99 to about 50 weight percent of the polymer, y can be from about 1 to about 50 weight percent of the polymer, and z ranges from about 0 to about 50 weight percent of the polymer. At least a portion of the neutralizable groups R_1 are neutralized. When the amount of z is greater than zero, a portion of the groups R_{10} can also be fully or partially neutralized, as desired.

In particular, the anionic polymers and blends thereof can comprise compatible blends of anionic polymers and ionomers, such as the ionomers described above, and ethylene acrylic methacrylic acid ionomers, and their terpolymers, sold commercially under the trade names SURLYN® and IOTEK® by DuPont and Exxon respectively. The anionic polymer blends useful in the golf balls of the invention can also include other polymers, such as polyvinylalcohol, copolymers of ethylene and vinyl alcohol, poly(ethylethylene), poly(heptylethylene), poly(hexyldecylethylene), poly(isopentylethylene), poly(butyl acrylate), acrylate, poly(2-ethylbutyl acrylate), poly(heptyl acrylate), poly(2-methylbutyl acrylate), poly(3-methylbutyl acrylate), poly(N-octadecylacrylamide), poly(octadecyl methacrylate), poly(butoxyethylene), poly(methoxyethylene), poly(pentyloxyethylene), poly(1,1-dichloroethylene), poly(4-[(2-butoxyethoxy)methyl]styrene), poly[oxy(ethoxymethyl)ethylene], poly(oxyethylethylene), poly(oxytetramethylene), poly(oxytrimethylene), poly(silanes) and poly(silazanes), polyamides, polycarbonates, polyesters, styrene block copolymers, polyetheramides, polyurethanes, main-chain heterocyclic polymers and poly(furan tetracarboxylic acid diimides), as well as the classes of polymers to which they belong.

The anionic polymer compositions of the present invention typically have a flexural modulus of from about 500 psi to about 300,000 psi, preferably from about 2000 to about 200,000 psi. The anionic polymer compositions typically have a material hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D. The loss tangent, or dissipation factor, is a ratio of the loss modulus over the dynamic shear storage modulus, and is typically less than about 1, preferably less than about 0.01, and more preferably less than about 0.001 for the anionic polymer compositions measured at about 23° C. The specific gravity is typically greater than about 0.7, preferably greater than about 1, for the anionic polymer compositions. The dynamic shear storage modulus, or storage modulus, of the anionic polymer compositions at about 23° C. is typically at least about 10,000 dyn/cm².

The golf balls of the present invention may comprise a variety of constructions. In one embodiment of the present invention, golf ball includes a core, an inner cover layer surrounding the core, and an outer cover layer. Preferably, the core is solid. More preferably, the core is a solid, single-layer core. In a preferred embodiment, the solid core comprises the HNP's of the present invention. In an alternative embodiment, the solid core may include compositions having a base rubber, a crosslinking agent, a filler, and a co-crosslinking or initiator agent, and the inner cover layer comprises the HNP's of the present invention.

The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene having a cis-structure of at least 40%. More preferably, the base rubber comprises high-Mooney-viscosity rubber. If desired, the polybutadiene can also be mixed with other elastomers

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known in the art such as natural rubber, polyisoprene rubber and/or styrene-butadiene rubber in order to modify the properties of the core.

The crosslinking agent includes a metal salt of an unsaturated fatty acid such as a zinc salt or a magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms such as acrylic or methacrylic acid. Suitable cross linking agents include metal salt diacrylates, dimethacrylates and monomethacrylates wherein the metal is magnesium, calcium, zinc, aluminum, sodium, lithium or nickel. The crosslinking agent is present in an amount from about 15 to about 40 parts per hundred of the rubber, preferably in an amount from about 19 to about 25 parts per hundred of the rubber and most preferably having about 20 to 24 parts crosslinking agent per hundred of rubber. The core compositions of the present invention may also include at least one organic or inorganic cis-trans catalyst to convert a portion of the cis-isomer of polybutadiene to the trans-isomer, as desired.

The initiator agent can be any known polymerization initiator which decomposes during the cure cycle. Suitable initiators include peroxide compounds such as dicumyl peroxide, 1,1-di-(t-butylperoxy) 3,3,5-trimethyl cyclohexane, a-a bis-(t-butylperoxy)diisopropylbenzene, 2,5-dimethyl-2,5 di-(t-butylperoxy)hexane or di-t-butyl peroxide and mixtures thereof.

Fillers, any compound or composition that can be used to vary the density and other properties of the core, typically include materials such as tungsten, zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate, metals, metal oxides and salts, regrind (recycled core material typically ground to about 30 mesh particle), high-Mooney-viscosity rubber regrind, and the like.

The HNP compositions of the present invention may also be moisture resistant. For purposes of the present disclosure, a composition is "moisture resistant" if it has a moisture vapor transmission rate ("MVTR") of 12.5 gmil/100 in²/day or less. Preferably, the moisture resistant compositions of the present invention have an MVTR of 8.0 gmil/100 in²/day or less, or 6.5 gmil/100 in²/day or less, or 5.0 gmil/100 in²/day or less, or 4.0 gmil/100 in²/day or less, or 2.5 gmil/100 in²/day or less, or 2.0 gmil/100 in²/day or less. As used herein, moisture vapor transmission rate (MVTR) is given in gmil/100 in²/day, and is measured at 20° C., and according to ASTM F1249-99.

In a particular embodiment, the cation source is selected from metal ions and compounds of calcium, metal ions and compounds of zinc, and combinations thereof. In a particular aspect of this embodiment, the equivalent percentage of calcium and/or zinc salt(s) in the final composition is 50% or higher, or 60% or higher, or 70% or higher, or 80% or higher, or 90% or higher, based on the total salts present in the final composition, wherein the equivalent % is determined by multiplying the mol % of the cation by the valence of the cation. In another particular embodiment, the cation source is selected from metal ions and compounds of lithium, sodium, potassium, magnesium, calcium, zinc, and combinations thereof. In another particular embodiment, the cation source is selected from metal ions and compounds of lithium, metal ions and compounds of zinc, and combinations thereof. Suitable cation sources also include mixtures of lithium and/or zinc cations with other cations. Other cations suitable for mixing with lithium and/or zinc cations to produce the HNP include, but are not limited to, the "less hydrophilic" cations disclosed in U.S. Patent Application Publication No. 2006/0106175; conventional HNP cations, such as those disclosed in U.S. Pat. Nos. 6,756,436 and 6,824,477; and the cations disclosed in U.S. Patent Application Publication No. 2005/

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0267240. The entire disclosure of each of these references is hereby incorporated herein by reference. In a particular aspect of this embodiment, the percentage of lithium and/or zinc salts in the composition is preferably 50% or higher, or 55% or higher, or 60% or higher, or 65% or higher, or 70% or higher, or 80% or higher, or 90% or higher, or 95% or higher, or 100%, based on the total salts present in the composition. The amount of cation source used is readily determined based on the desired level of neutralization.

The golf ball cores of the present invention may also comprise a variety of constructions. For example, the core may comprise a single layer or a plurality of layers. The core may also comprise a layer of tensioned elastomeric material. In another embodiment of the present invention, golf ball comprises a solid center surrounded by at least one additional solid outer core layer. The "dual" core is surrounded by a "double" cover comprising an inner cover layer and an outer cover layer.

Preferably, the solid center comprises the HNP's of the present invention. In another embodiment, the inner cover layer comprises the highly-neutralized acid copolymers of the present invention. In an alternative embodiment, the outer core layer comprises the highly-neutralized acid copolymers of the present invention.

At least one of the outer core layers is formed of a resilient rubber-based component comprising a high-Mooney-viscosity rubber, and a crosslinking agent present in an amount from about 20 to about 40 parts per hundred, from about 30 to about 38 parts per hundred, and most preferably about 37 parts per hundred. It should be understood that the term "parts per hundred" is with reference to the rubber by weight.

When the golf ball of the present invention includes an intermediate layer, such as an outer core layer or an inner cover layer, any or all of these layer(s) may comprise thermoplastic and thermosetting material, but preferably the intermediate layer(s), if present, comprise any suitable material, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid which are available under the trademark SURLYN® of E.I. DuPont de Nemours & Co., of Wilmington, Del., or IOTEK® or ESCOR® of Exxon. These are copolymers or terpolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel or the like, in which the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include methacrylic, crotonic, maleic, fumaric or itaconic acid.

This golf ball can likewise include one or more homopolymeric or copolymeric inner cover materials, such as:

- (1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;
- (2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst;
- (3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates, in particular PPDI-based thermoplastic polyurethanes, and those disclosed in U.S. Pat. No. 5,334,673;

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- (4) Polyureas, such as those disclosed in U.S. Pat. No. 5,484,870;
- (5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly(caprolactam), and blends of polyamides with SURLYN®, polyethylene, ethylene copolymers, ethylene-propylene-non-conjugated diene terpolymer, and the like;
- (6) Acrylic resins and blends of these resins with poly vinyl chloride, elastomers, and the like;
- (7) Thermoplastics, such as urethane; olefinic thermoplastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer; block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly(ether-amide), such as PEBAX®, sold by ELF Atochem of Philadelphia, Pa.;
- (8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene as sold under the trademark NORYL® by General Electric Company of Pittsfield, Mass.;
- (9) Thermoplastic polyesters, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified, poly(trimethylene terephthalate), and elastomers sold under the trademarks HYTREL® by E.I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD® by General Electric Company of Pittsfield, Mass.;
- (10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene or ethylene vinyl acetate or other elastomers; and
- (11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

Preferably, the inner cover includes polymers, such as ethylene, propylene, butene-1 or hexane-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. More preferably, in a low spin rate embodiment designed for maximum distance, the acrylic or methacrylic acid is present in about 16 to 35 weight percent, making the ionomer a high modulus ionomer. In a higher spin embodiment, the inner cover layer includes an ionomer where an acid is present in about 10 to 15 weight percent and includes a softening comonomer. Additionally, high-density polyethylene ("HDPE"), low-density polyethylene ("LDPE"), LLDPE, and homo- and co-polymers of polyolefin are suitable for a variety of golf ball layers.

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In one embodiment, the outer cover preferably includes a polyurethane composition comprising the reaction product of at least one polyisocyanate, polyol, and at least one curing agent. Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"); polymeric MDI; carbodiimide-modified liquid MDI; 4,4'-dicyclohexylmethane diisocyanate ("H₁₂MDI"); p-phenylene diisocyanate ("PPDI"); m-phenylene diisocyanate ("MPDI"); toluene diisocyanate ("TDI"); 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"); isophoronediiisocyanate ("IPDI"); hexamethylene diisocyanate ("HDI"); naphthalene diisocyanate ("NDI"); xylene diisocyanate ("XDI"); p-tetramethylxylene diisocyanate ("p-TMXDI"); m-tetramethylxylene diisocyanate ("m-TMXDI"); ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate ("TMDI"); tetracene diisocyanate; naphthalene diisocyanate; anthracene diisocyanate; isocyanurate of toluene diisocyanate; uretdione of hexamethylene diisocyanate; and mixtures thereof. Polyisocyanates are known to those of ordinary skill in the art as having more than one isocyanate group, e.g., di-isocyanate, tri-isocyanate, and tetra-isocyanate. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term "MDI" includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 7.5% NCO, and more preferably, less than about 7.0%.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol. Examples include, but are not limited to, polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

In another embodiment, polyester polyols are included in the polyurethane material of the invention. Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol; polybutylene adipate glycol; polyethylene propylene adipate glycol; o-phthalate-1,6-hexanediol; poly(hexamethylene adipate) glycol; and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

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In another embodiment, polycaprolactone polyols are included in the materials of the invention. Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In yet another embodiment, the polycarbonate polyols are included in the polyurethane material of the invention. Suitable polycarbonates include, but are not limited to, polyphthalate carbonate and poly(hexamethylene carbonate) glycol. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups. In one embodiment, the molecular weight of the polyol is from about 200 to about 4000.

Polyamine curatives are also suitable for use in the polyurethane composition of the invention and have been found to improve cut, shear, and impact resistance of the resultant balls. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline) ("MCDEA"); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyl-diamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine ("MPDA"); 4,4'-methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-methylene-bis-(2,6-diethylaniline) ("MDEA"); 4,4'-methylene-bis-(2,3-dichloroaniline) ("MDCA"); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as ETHACURE 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives, which include both primary and secondary amines, preferably have molecular weights ranging from about 64 to about 2000.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β-hydroxyethyl)ether; hydroquinone-di-(β-hydroxyethyl) ether; and mixtures thereof. Preferred hydroxy-terminated curatives include 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol, and mixtures thereof. Preferably, the hydroxy-terminated curatives have molecular weights ranging from about 48 to 2000. It should be understood that molecular weight, as used herein, is the absolute weight average molecular weight and would be understood as such by one of ordinary skill in the art.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or

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mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

In a preferred embodiment of the present invention, saturated polyurethanes used to form cover layers, preferably the outer cover layer, and may be selected from among both castable thermoset and thermoplastic polyurethanes.

In this embodiment, the saturated polyurethanes of the present invention are substantially free of aromatic groups or moieties. Saturated polyurethanes suitable for use in the invention are a product of a reaction between at least one polyurethane prepolymer and at least one saturated curing agent. The polyurethane prepolymer is a product formed by a reaction between at least one saturated polyol and at least one saturated diisocyanate. As is well known in the art, a catalyst may be employed to promote the reaction between the curing agent and the isocyanate and polyol.

Saturated diisocyanates which can be used include, without limitation, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; dicyclohexylmethane diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isophorone diisocyanate ("IPDI"); methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate ("TMDI"). The most preferred saturated diisocyanates are 4,4'-dicyclohexylmethane diisocyanate ("HMDI") and isophorone diisocyanate ("IPDI").

Saturated polyols which are appropriate for use in this invention include without limitation polyether polyols such as polytetramethylene ether glycol and poly(oxypropylene) glycol. Suitable saturated polyester polyols include polyethylene adipate glycol, polyethylene propylene adipate glycol, polybutylene adipate glycol, polycarbonate polyol and ethylene oxide-capped polyoxypropylene diols. Saturated polycaprolactone polyols which are useful in the invention include diethylene glycol-initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, 1,6-hexanediol-initiated polycaprolactone; trimethylol propane-initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, and polytetramethylene ether glycol-initiated polycaprolactone. The most preferred saturated polyols are polytetramethylene ether glycol and PTMEG-initiated polycaprolactone.

Suitable saturated curatives include 1,4-butanediol, ethylene glycol, diethylene glycol, polytetramethylene ether glycol, propylene glycol; trimethanolpropane; tetra-(2-hydroxypropyl)-ethylenediamine; isomers and mixtures of isomers of cyclohexyldimethylol, isomers and mixtures of isomers of cyclohexane bis(methylamine); triisopropanolamine; ethylene diamine; diethylene triamine; triethylene tetramine; tetraethylene pentamine; 4,4'-dicyclohexylmethane diamine; 2,2,4-trimethyl-1,6-hexanediamine; 2,4,4-trimethyl-1,6-hexanediamine; diethyleneglycol di-(aminopropyl)ether; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,2-bis-(sec-butylamino)cyclohexane; 1,4-bis-(sec-butylamino)cyclohexane; isophorone diamine; hexamethylene diamine; propylene diamine; 1-methyl-2,4-cyclohexyl diamine; 1-methyl-2,6-cyclohexyl diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; imido-bis-propylamine; isomers and mixtures of isomers of diaminocyclohexane; monoethanolamine; diethanolamine; triethanolamine; monoisopropanolamine; and diisopropanolamine. The most preferred saturated curatives are 1,4-butanediol, 1,4-cyclohexyldimethylol and 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

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The compositions of the invention may also be polyurea-based, which are distinctly different from polyurethane compositions, but also result in desirable aerodynamic and aesthetic characteristics when used in golf ball components. The polyurea-based compositions are preferably saturated in nature.

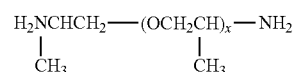
Without being bound to any particular theory, it is now believed that substitution of the long chain polyol segment in the polyurethane prepolymer with a long chain polyamine oligomer soft segment to form a polyurea prepolymer, improves shear, cut, and resiliency, as well as adhesion to other components. Thus, the polyurea compositions of this invention may be formed from the reaction product of an isocyanate and polyamine prepolymer crosslinked with a curing agent. For example, polyurea-based compositions of the invention may be prepared from at least one isocyanate, at least one polyether amine, and at least one diol curing agent or at least one diamine curing agent.

Any polyamine available to one of ordinary skill in the art is suitable for use in the polyurea prepolymer. Polyether amines are particularly suitable for use in the prepolymer. As used herein, "polyether amines" refer to at least polyoxyalkyleneamines containing primary amino groups attached to the terminus of a polyether backbone. Due to the rapid reaction of isocyanate and amine, and the insolubility of many urea products, however, the selection of diamines and polyether amines is limited to those allowing the successful formation of the polyurea prepolymers. In one embodiment, the polyether backbone is based on tetramethylene, propylene, ethylene, trimethylolpropane, glycerin, and mixtures thereof.

Suitable polyether amines include, but are not limited to, methyldiethanolamine; polyoxyalkylenediamines such as, polytetramethylene ether diamines, polyoxypropylenetriamine, and polyoxypropylene diamines; poly(ethylene oxide capped oxypropylene)ether diamines; propylene oxide-based triamines; triethyleneglycoldiamines; trimethylolpropane-based triamines; glycerin-based triamines; and mixtures thereof. In one embodiment, the polyether amine used to form the prepolymer is JEFFAMINE® D2000 (manufactured by Huntsman Chemical Co. of Austin, Tex.).

The molecular weight of the polyether amine for use in the polyurea prepolymer may range from about 100 to about 5000. As used herein, the term "about" is used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range. In one embodiment, the polyether amine molecular weight is about 200 or greater, preferably about 230 or greater. In another embodiment, the molecular weight of the polyether amine is about 4000 or less. In yet another embodiment, the molecular weight of the polyether amine is about 600 or greater. In still another embodiment, the molecular weight of the polyether amine is about 3000 or less. In yet another embodiment, the molecular weight of the polyether amine is between about 1000 and about 3000, and more preferably is between about 1500 to about 2500. Because lower molecular weight polyether amines may be prone to forming solid polyureas, a higher molecular weight oligomer, such as Jeffamine D2000, is preferred.

In one embodiment, the polyether amine has the generic structure:

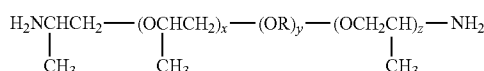


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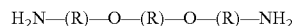
wherein the repeating unit x has a value ranging from about 1 to about 70. Even more preferably, the repeating unit may be from about 5 to about 50, and even more preferably is from about 12 to about 35.

In another embodiment, the polyether amine has the generic structure:



wherein the repeating units x and z have combined values from about 3.6 to about 8 and the repeating unit y has a value ranging from about 9 to about 50, and wherein R is $\text{---}(\text{CH}_2)_a\text{---}$, where "a" may be a repeating unit ranging from about 1 to about 10.

In yet another embodiment, the polyether amine has the generic structure:



wherein R is $\text{---}(\text{CH}_2)_a\text{---}$, and "a" may be a repeating unit ranging from about 1 to about 10.

As briefly discussed above, some amines may be unsuitable for reaction with the isocyanate because of the rapid reaction between the two components. In particular, shorter chain amines are fast reacting. In one embodiment, however, a hindered secondary diamine may be suitable for use in the prepolymer. Without being bound to any particular theory, it is believed that an amine with a high level of steric hindrance, e.g., a tertiary butyl group on the nitrogen atom, has a slower reaction rate than an amine with no hindrance or a low level of hindrance. For example, 4,4'-bis-(sec-butylamino)-dicyclohexylmethane (CLEARLINK® 1000) may be suitable for use in combination with an isocyanate to form the polyurea prepolymer.

Any isocyanate available to one of ordinary skill in the art is suitable for use in the polyurea prepolymer. Isocyanates for use with the present invention include aliphatic, cycloaliphatic, araliphatic, aromatic, any derivatives thereof, and combinations of these compounds having two or more isocyanate (NCO) groups per molecule. The isocyanates may be organic polyisocyanate-terminated prepolymers. The isocyanate-containing reactable component may also include any isocyanate-functional monomer, dimer, trimer, or multimeric adduct thereof, prepolymer, quasi-prepolymer, or mixtures thereof. Isocyanate-functional compounds may include monoisocyanates or polyisocyanates that include any isocyanate functionality of two or more.

Suitable isocyanate-containing components include diisocyanates having the generic structure: $\text{O}=\text{C}=\text{N---R---N}=\text{C}=\text{O}$, where R is preferably a cyclic, aromatic, or linear or branched hydrocarbon moiety containing from about 1 to about 20 carbon atoms. The diisocyanate may also contain one or more cyclic groups or one or more phenyl groups. When multiple cyclic or aromatic groups are present, linear and/or branched hydrocarbons containing from about 1 to about 10 carbon atoms can be present as spacers between the cyclic or aromatic groups. In some cases, the cyclic or aromatic group(s) may be substituted at the 2-, 3-, and/or 4-positions, or at the ortho-, meta-, and/or para-positions, respectively. Substituted groups may include, but are not limited to, halogens, primary, secondary, or tertiary hydrocarbon groups, or a mixture thereof.

Examples of diisocyanates that can be used with the present invention include, but are not limited to, substituted and isomeric mixtures including 2,2'-, 2,4'-, and 4,4'-diphenylmethane diisocyanate (MDI); 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI); toluene diisocyanate (TDI); polymeric MDI; carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate; para-phenylene diisocyanate (PPDI); meta-phenylene diisocyanate (MPDI); triphenyl methane-4,4'- and triphenyl methane-4,4'-triisocyanate; naphthylene-1,5-diisocyanate; 2,4'-, 4,4'-, and 2,2-biphenyl diisocyanate; polyphenyl polymethylene polyisocyanate (PMDI); mixtures of MDI and PMDI; mixtures of PMDI and TDI; ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,2-diisocyanate; tetramethylene-1,3-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate (HDI); octamethylene diisocyanate; decamethylene diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl-cyclohexylene diisocyanate (HTDI); 2,4-methylcyclohexane diisocyanate; 2,6-methylcyclohexane diisocyanate; 4,4'-dicyclohexyl diisocyanate; 1,3,5-cyclohexane triisocyanate; isocyanatomethylcyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isocyanatoethylcyclohexane isocyanate; bis(isocyanatomethyl)-cyclohexane diisocyanate; 4,4'-bis(isocyanatomethyl)dicyclohexane; 2,4'-bis(isocyanatomethyl)dicyclohexane; isophorone diisocyanate (IPDI); triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate (TMDI); 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI); 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; aromatic aliphatic isocyanate, such as 1,2-, 1,3-, and 1,4-xylylene diisocyanate; meta-tetramethylxylylene diisocyanate (m-TMXDI); para-tetramethylxylylene diisocyanate (p-TMXDI); trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylxylylene diisocyanate, isocyanurate of hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate, and mixtures thereof; dimerized uredione of any polyisocyanate, such as uredione of toluene diisocyanate, uredione of hexamethylene diisocyanate, and mixtures thereof; modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof.

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nylmethane diisocyanate (MDI); 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI); toluene diisocyanate (TDI); polymeric MDI; carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate; para-phenylene diisocyanate (PPDI); meta-phenylene diisocyanate (MPDI); triphenyl methane-4,4'- and triphenyl methane-4,4'-triisocyanate; naphthylene-1,5-diisocyanate; 2,4'-, 4,4'-, and 2,2-biphenyl diisocyanate; polyphenyl polymethylene polyisocyanate (PMDI); mixtures of MDI and PMDI; mixtures of PMDI and TDI; ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,2-diisocyanate; tetramethylene-1,3-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate (HDI); octamethylene diisocyanate; decamethylene diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl-cyclohexylene diisocyanate (HTDI); 2,4-methylcyclohexane diisocyanate; 2,6-methylcyclohexane diisocyanate; 4,4'-dicyclohexyl diisocyanate; 1,3,5-cyclohexane triisocyanate; isocyanatomethylcyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isocyanatoethylcyclohexane isocyanate; bis(isocyanatomethyl)-cyclohexane diisocyanate; 4,4'-bis(isocyanatomethyl)dicyclohexane; 2,4'-bis(isocyanatomethyl)dicyclohexane; isophorone diisocyanate (IPDI); triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate (TMDI); 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI); 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; 1,2-, 1,3-, and 1,4-phenylene diisocyanate; aromatic aliphatic isocyanate, such as 1,2-, 1,3-, and 1,4-xylylene diisocyanate; meta-tetramethylxylylene diisocyanate (m-TMXDI); para-tetramethylxylylene diisocyanate (p-TMXDI); trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylxylylene diisocyanate, isocyanurate of hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate, and mixtures thereof; dimerized uredione of any polyisocyanate, such as uredione of toluene diisocyanate, uredione of hexamethylene diisocyanate, and mixtures thereof; modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof.

Examples of saturated diisocyanates that can be used with the present invention include, but are not limited to, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate (HDI); octamethylene diisocyanate; decamethylene diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl-cyclohexylene diisocyanate (HTDI); 2,4-methylcyclohexane diisocyanate; 2,6-methylcyclohexane diisocyanate; 4,4'-dicyclohexyl diisocyanate; 2,4'-dicyclohexyl diisocyanate; 1,3,5-cyclohexane triisocyanate; isocyanatomethylcyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isocyanatoethylcyclohexane isocyanate; bis(isocyanatomethyl)-cyclohexane diisocyanate; 4,4'-bis(isocyanatomethyl)dicyclohexane; 2,4'-bis(isocyanatomethyl)dicyclohexane; isophorone diisocyanate (IPDI); triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate (TMDI); 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI); 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; and mixtures thereof. Aromatic aliphatic isocyanates may also be

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used to form light stable materials. Examples of such isocyanates include 1,2-, 1,3-, and 1,4-xylene diisocyanate; meta-tetramethylxylene diisocyanate (m-TMXDI); para-tetramethylxylene diisocyanate (p-TMXDI); trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylxylene diisocyanate, isocyanurate of hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate, and mixtures thereof; dimerized uretdione of any polyisocyanate, such as uretdione of toluene diisocyanate, uretdione of hexamethylene diisocyanate, and mixtures thereof; modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof. In addition, the aromatic aliphatic isocyanates may be mixed with any of the saturated isocyanates listed above for the purposes of this invention.

The number of unreacted NCO groups in the polyurea prepolymer of isocyanate and polyether amine may be varied to control such factors as the speed of the reaction, the resultant hardness of the composition, and the like. For instance, the number of unreacted NCO groups in the polyurea prepolymer of isocyanate and polyether amine may be less than about 14 percent. In one embodiment, the polyurea prepolymer has from about 5 percent to about 11 percent unreacted NCO groups, and even more preferably has from about 6 to about 9.5 percent unreacted NCO groups. In one embodiment, the percentage of unreacted NCO groups is about 3 percent to about 9 percent. Alternatively, the percentage of unreacted NCO groups in the polyurea prepolymer may be about 7.5 percent or less, and more preferably, about 7 percent or less. In another embodiment, the unreacted NCO content is from about 2.5 percent to about 7.5 percent, and more preferably from about 4 percent to about 6.5 percent.

When formed, polyurea prepolymers may contain about 10 percent to about 20 percent by weight of the prepolymer of free isocyanate monomer. Thus, in one embodiment, the polyurea prepolymer may be stripped of the free isocyanate monomer. For example, after stripping, the prepolymer may contain about 1 percent or less free isocyanate monomer. In another embodiment, the prepolymer contains about 0.5 percent by weight or less of free isocyanate monomer.

The polyether amine may be blended with additional polyols to formulate copolymers that are reacted with excess isocyanate to form the polyurea prepolymer. In one embodiment, less than about 30 percent polyol by weight of the copolymer is blended with the saturated polyether amine. In another embodiment, less than about 20 percent polyol by weight of the copolymer, preferably less than about 15 percent by weight of the copolymer, is blended with the polyether amine. The polyols listed above with respect to the polyurethane prepolymer, e.g., polyether polyols, polycaprolactone polyols, polyester polyols, polycarbonate polyols, hydrocarbon polyols, other polyols, and mixtures thereof, are also suitable for blending with the polyether amine. The molecular weight of these polymers may be from about 200 to about 4000, but also may be from about 1000 to about 2500, and more preferably are from about 1500 to about 2500.

The polyurea composition can be formed by crosslinking the polyurea prepolymer with a single curing agent or a blend of curing agents. The curing agent of the invention is preferably an amine-terminated curing agent, more preferably a secondary diamine curing agent so that the composition contains only urea linkages. In one embodiment, the amine-terminated curing agent may have a molecular weight of about 64 or greater. In another embodiment, the molecular weight of the amine-curing agent is about 2000 or less. As discussed above, certain amine-terminated curing agents may

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be modified with a compatible amine-terminated freezing point depressing agent or mixture of compatible freezing point depressing agents.

Suitable amine-terminated curing agents include, but are not limited to, ethylene diamine; hexamethylene diamine; 1-methyl-2,6-cyclohexyl diamine; tetrahydroxypropylene ethylene diamine; 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 4,4'-dicyclohexylmethane diamine; 1,4-cyclohexane-bis-(methylamine); 1,3-cyclohexane-bis-(methylamine); diethylene glycol di-(aminopropyl)ether; 2-methylpentamethylene-diamine; diaminocyclohexane; diethylene triamine; triethylene tetramine; tetraethylene pentamine; propylene diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; dipropylene triamine; imido-bis-propylamine; monoethanolamine, diethanolamine; triethanolamine; monoisopropanolamine, diisopropanolamine; isophoronediamine; 4,4'-methylenebis-(2-chloroaniline); 3,5; dimethylthio-2,4-toluenediamine; 3,5-dimethylthio-2,6-toluenediamine; 3,5-diethylthio-2,4-toluenediamine; 3,5; diethylthio-2,6-toluenediamine; 4,4'-bis-(sec-butylamino)-diphenylmethane and derivatives thereof 1,4-bis-(sec-butylamino)-benzene; 1,2-bis-(sec-butylamino)-benzene; N,N'-dialkylamino-diphenylmethane; N,N,N',N'-tetrakis(2-hydroxypropyl)ethylene diamine; trimethyleneglycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; 4,4'-methylenebis-(3-chloro-2,6-diethylenedianiline); 4,4'-methylenebis-(2,6-diethylaniline); meta-phenylenediamine; paraphenylenediamine; and mixtures thereof. In one embodiment, the amine-terminated curing agent is 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

Suitable saturated amine-terminated curing agents include, but are not limited to, ethylene diamine; hexamethylene diamine; 1-methyl-2,6-cyclohexyl diamine; tetrahydroxypropylene ethylene diamine; 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 4,4'-dicyclohexylmethane diamine; 4,4'-methylenebis-(2,6-diethylaminocyclohexane); 1,4-cyclohexane-bis-(methylamine); 1,3-cyclohexane-bis-(methylamine); diethylene glycol di-(aminopropyl)ether; 2-methylpentamethylene-diamine; diaminocyclohexane; diethylene triamine; triethylene tetramine; tetraethylene pentamine; propylene diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; imido-bis-propylamine; monoethanolamine, diethanolamine; triethanolamine; monoisopropanolamine, diisopropanolamine; isophoronediamine; triisopropanolamine; and mixtures thereof. In addition, any of the polyether amines listed above may be used as curing agents to react with the polyurea prepolymers.

Suitable catalysts include, but are not limited to bismuth catalyst, oleic acid, triethylenediamine (DABCO®-33LV), di-butyltin dilaurate (DABCO®-T12) and acetic acid. The most preferred catalyst is di-butyltin dilaurate (DABCO®-T12). DABCO® materials are manufactured by Air Products and Chemicals, Inc.

Thermoplastic materials may be blended with other thermoplastic materials, but thermosetting materials are difficult if not impossible to blend homogeneously after the thermosetting materials are formed. Preferably, the saturated polyurethane comprises from about 1% to about 100%, more preferably from about 10% to about 75% of the cover com-

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position and/or the intermediate layer composition. About 90% to about 10%, more preferably from about 90% to about 25% of the cover and/or the intermediate layer composition is comprised of one or more other polymers and/or other materials as described below. Such polymers include, but are not limited to polyurethane/polyurea ionomers, polyurethanes or polyureas, epoxy resins, polyethylenes, polyamides and polyesters, polycarbonates and polyacrylin. Unless otherwise stated herein, all percentages are given in percent by weight of the total composition of the golf ball layer in question.

Polyurethane prepolymers are produced by combining at least one polyol, such as a polyether, polycaprolactone, polycarbonate or a polyester, and at least one isocyanate. Thermosetting polyurethanes are obtained by curing at least one polyurethane prepolymer with a curing agent selected from a polyamine, triol or tetraol. Thermoplastic polyurethanes are obtained by curing at least one polyurethane prepolymer with a diol curing agent. The choice of the curatives is critical because some urethane elastomers that are cured with a diol and/or blends of diols do not produce urethane elastomers with the impact resistance required in a golf ball cover. Blending the polyamine curatives with diol cured urethane elastomeric formulations leads to the production of thermoset urethanes with improved impact and cut resistance.

Thermoplastic polyurethanes may be blended with suitable materials to produce a thermoplastic end product. Examples of such additional materials may include ionomers such as the SURLYN®, ESCOR® and IOTEK® copolymers described above.

Other suitable materials which may be combined with the saturated polyurethanes in forming the cover and/or intermediate layer(s) of the golf balls of the invention include ionic or non-ionic polyurethanes and polyureas, epoxy resins, polyethylenes, polyamides and polyesters. For example, the cover and/or intermediate layer may be formed from a blend of at least one saturated polyurethane and thermoplastic or thermoset ionic and non-ionic urethanes and polyurethanes, cationic urethane ionomers and urethane epoxies, ionic and non-ionic polyureas and blends thereof. Examples of suitable urethane ionomers are disclosed in U.S. Pat. No. 5,692,974 entitled "Golf Ball Covers", the disclosure of which is hereby incorporated by reference in its entirety. Other examples of suitable polyurethanes are described in U.S. Pat. No. 5,334,673. Examples of appropriate polyureas are discussed in U.S. Pat. No. 5,484,870 and examples of suitable polyurethanes cured with epoxy group containing curing agents are disclosed in U.S. Pat. No. 5,908,358, the disclosures of which are hereby incorporated herein by reference in their entirety.

A variety of conventional components can be added to the cover compositions of the present invention. These include, but are not limited to, white pigment such as TiO₂, ZnO, optical brighteners, surfactants, processing aids, foaming agents, density-controlling fillers, UV stabilizers and light stabilizers. Saturated polyurethanes are resistant to discoloration. However, they are not immune to deterioration in their mechanical properties upon weathering. Addition of UV absorbers and light stabilizers therefore helps to maintain the tensile strength and elongation of the saturated polyurethane elastomers. Suitable UV absorbers and light stabilizers include TINUVIN® 328, TINUVIN® 213, TINUVIN® 765, TINUVIN® 770 and TINUVIN® 622. The preferred UV absorber is TINUVIN® 328, and the preferred light stabilizer is TINUVIN® 765. TINUVIN® products are available from Ciba-Geigy. Dyes, as well as optical brighteners and fluorescent pigments may also be included in the golf ball covers produced with polymers formed according to the present

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invention. Such additional ingredients may be added in any amounts that will achieve their desired purpose.

Any method known to one of ordinary skill in the art may be used to polyurethanes of the present invention. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogenous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition. Other methods suitable for forming the layers of the present invention include reaction injection molding ("RIM"), liquid injection molding ("LIM"), and pre-reacting the components to form an injection moldable thermoplastic polyurethane and then injection molding, all of which are known to one of ordinary skill in the art.

Additional components which can be added to the polyurethane composition include UV stabilizers and other dyes, as well as optical brighteners and fluorescent pigments and dyes. Such additional ingredients may be added in any amounts that will achieve their desired purpose. It has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the urethane elastomer material can be applied over the core using a variety of application techniques such as spraying, dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Pat. No. 5,733,428, the disclosure of which is hereby incorporated by reference in its entirety.

The outer cover is preferably formed around the inner cover by mixing and introducing the material in the mold halves. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing cores into the mold halves is determined to be approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using centering pins moving into holes in each mold. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity. After the reacting materials have resided in top mold halves for about 40 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture.

A ball cup holds the ball core through reduced pressure (or partial vacuum). Upon location of the coated core in the halves of the mold after gelling for about 40 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit, inverted and mated with other mold halves which, at an appropriate time

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earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

Similarly, U.S. Pat. No. 5,006,297 to Brown et al. and U.S. Pat. No. 5,334,673 to Wu both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. Further, U.S. Pat. Nos. 6,180,040 and 6,180,722 disclose methods of preparing dual core golf balls. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

Depending on the desired properties, balls prepared according to the invention can exhibit substantially the same or higher resilience, or coefficient of restitution ("COR"), with a decrease in compression or modulus, compared to balls of conventional construction. Additionally, balls prepared according to the invention can also exhibit substantially higher resilience, or COR, without an increase in compression, compared to balls of conventional construction. Another measure of this resilience is the "loss tangent," or $\tan \delta$, which is obtained when measuring the dynamic stiffness of an object. Loss tangent and terminology relating to such dynamic properties is typically described according to ASTM D4092-90. Thus, a lower loss tangent indicates a higher resiliency, thereby indicating a higher rebound capacity. Low loss tangent indicates that most of the energy imparted to a golf ball from the club is converted to dynamic energy, i.e., launch velocity and resulting longer distance. The rigidity or compressive stiffness of a golf ball may be measured, for example, by the dynamic stiffness. A higher dynamic stiffness indicates a higher compressive stiffness. To produce golf balls having a desirable compressive stiffness, the dynamic stiffness of the crosslinked reaction product material should be less than about 50,000 N/m at -50°C . Preferably, the dynamic stiffness should be between about 10,000 and 40,000 N/m at -50°C ., more preferably, the dynamic stiffness should be between about 20,000 and 30,000 N/m at -50°C .

The molding process and composition of golf ball portions typically results in a gradient of material properties. Methods employed in the prior art generally exploit hardness to quantify these gradients. Hardness is a qualitative measure of static modulus and does not represent the modulus of the material at the deformation rates associated with golf ball use, i.e., impact by a club. As is well known to one skilled in the art of polymer science, the time-temperature superposition principle may be used to emulate alternative deformation rates. For golf ball portions including polybutadiene, a 1-Hz oscillation at temperatures between 0°C . and -50°C . are believed to be qualitatively equivalent to golf ball impact rates. Therefore, measurement of loss tangent and dynamic stiffness at 0°C . to -50°C . may be used to accurately anticipate golf ball performance, preferably at temperatures between about -20°C . and -50°C .

In another embodiment of the present invention, a golf ball of the present invention is substantially spherical and has a cover with a plurality of dimples formed on the outer surface thereof.

U.S. application Ser. No. 10/230,015, now U.S. Publication No. 2003/0114565, and U.S. application Ser. No. 10/108,793, now U.S. Publication No. 2003/0050373, which are incorporated by reference herein in their entirety, discuss soft, high resilient ionomers, which are preferably from neutralizing the acid copolymer(s) of at least one E/X/Y copolymer, where E is ethylene, X is the α,β -ethylenically unsaturated carboxylic acid, and Y is a softening co-monomer. X is preferably present in 2-30 (preferably 4-20, most preferably 5-15)

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wt. % of the polymer, and Y is preferably present in 17-40 (preferably 20-40, and more preferably 24-35) wt. % of the polymer. Preferably, the melt index (MI) of the base resin is at least 20, or at least 40, more preferably, at least 75 and most preferably at least 150. Particular soft, resilient ionomers included in this invention are partially neutralized ethylene/(meth)acrylic acid/butyl(meth)acrylate copolymers having an MI and level of neutralization that results in a melt processible polymer that has useful physical properties. The copolymers are at least partially neutralized. Preferably at least 40, or, more preferably at least 55, even more preferably about 70, and most preferably about 80 of the acid moiety of the acid copolymer is neutralized by one or more alkali metal, transition metal, or alkaline earth metal cations. Cations useful in making the ionomers of this invention comprise lithium, sodium, potassium, magnesium, calcium, barium, or zinc, or a combination of such cations.

The invention also relates to a "modified" soft, resilient thermoplastic ionomer that comprises a melt blend of (a) the acid copolymers or the melt processible ionomers made therefrom as described above and (b) one or more organic acid(s) or salt(s) thereof, wherein greater than 80%, preferably greater than 90% of all the acid of (a) and of (b) is neutralized. Preferably, 100% of all the acid of (a) and (b) is neutralized by a cation source. Preferably, an amount of cation source in excess of the amount required to neutralize 100% of the acid in (a) and (b) is used to neutralize the acid in (a) and (b). Blends with fatty acids or fatty acid salts are preferred.

The organic acids or salts thereof are added in an amount sufficient to enhance the resilience of the copolymer. Preferably, the organic acids or salts thereof are added in an amount sufficient to substantially remove remaining ethylene crystallinity of the copolymer.

Preferably, the organic acids or salts are added in an amount of at least about 5% (weight basis) of the total amount of copolymer and organic acid(s). More preferably, the organic acids or salts thereof are added in an amount of at least about 15%, even more preferably at least about 20%. Preferably, the organic acid(s) are added in an amount up to about 50% (weight basis) based on the total amount of copolymer and organic acid. More preferably, the organic acids or salts thereof are added in an amount of up to about 40%, more preferably, up to about 35%. The non-volatile, non-migratory organic acids preferably are one or more aliphatic, mono-functional organic acids or salts thereof as described below, particularly one or more aliphatic, mono-functional, saturated or unsaturated organic acids having less than 36 carbon atoms or salts of the organic acids, preferably stearic acid or oleic acid. Fatty acids or fatty acid salts are most preferred.

Processes for fatty acid (salt) modifications are known in the art. Particularly, the modified highly-neutralized soft, resilient acid copolymer ionomers of this invention can be produced by:

(a) melt-blending (1) ethylene, α,β -ethylenically unsaturated C_{3-8} carboxylic acid copolymer(s) or melt-processible ionomer(s) thereof that have their crystallinity disrupted by addition of a softening monomer or other means with (2) sufficient non-volatile, non-migratory organic acids to substantially enhance the resilience and to disrupt (preferably remove) the remaining ethylene crystallinity, and then concurrently or subsequently.

(b) adding a sufficient amount of a cation source to increase the level of neutralization of all the acid moieties (including those in the acid copolymer and in the organic acid if the non-volatile, non-migratory organic acid is an organic acid) to the desired level.

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The weight ratio of X to Y in the composition is at least about 1:20. Preferably, the weight ratio of X to Y is at least about 1:15, more preferably, at least about 1:10. Furthermore, the weight ratio of X to Y is up to about 1:1.67, more preferably up to about 1:2. Most preferably, the weight ratio of X to Y in the composition is up to about 1:2.2.

The acid copolymers used in the present invention to make the ionomers are preferably 'direct' acid copolymers (containing high levels of softening monomers). As noted above, the copolymers are at least partially neutralized, preferably at least about 40% of X in the composition is neutralized. More preferably, at least about 55% of X is neutralized. Even more preferably, at least about 70, and most preferably, at least about 80% of X is neutralized. In the event that the copolymer is highly neutralized (e.g., to at least 45%, preferably 50%, 55%, 70%, or 80%, of acid moiety), the MI of the acid copolymer should be sufficiently high so that the resulting neutralized resin has a measurable MI in accord with ASTM D-1238, condition E, at 190° C., using a 2160 gram weight. Preferably this resulting MI will be at least 0.1, preferably at least 0.5, and more preferably 1.0 or greater. Preferably, for highly neutralized acid copolymer, the MI of the acid copolymer base resin is at least 20, or at least 40, at least 75, and more preferably at least 150.

The acid copolymers preferably comprise alpha olefin, particularly ethylene, C₃₋₈. α,β -ethylenically unsaturated carboxylic acid, particularly acrylic and methacrylic acid, and softening monomers, selected from alkyl acrylate, and alkyl methacrylate, wherein the alkyl groups have from 1-8 carbon atoms, copolymers. By "softening," it is meant that the crystallinity is disrupted (the polymer is made less crystalline). While the alpha olefin can be a C₂-C₄ alpha olefin, ethylene is most preferred for use in the present invention. Accordingly, it is described and illustrated herein in terms of ethylene as the alpha olefin.

The acid copolymers, when the alpha olefin is ethylene, can be described as E/X/Y copolymers where E is ethylene, X is the α,β -ethylenically unsaturated carboxylic acid, and Y is a softening comonomer; X is preferably present in 2-30 (preferably 4-20, most preferably 5-15) wt. % of the polymer, and Y is preferably present in 17-40 (preferably 20-40, most preferably 24-35) wt. % of the polymer.

The ethylene-acid copolymers with high levels of acid (X) are difficult to prepare in continuous polymerizers because of monomer-polymer phase separation. This difficulty can be avoided however by use of "co-solvent technology" as described in U.S. Pat. No. 5,028,674, or by employing somewhat higher pressures than those which copolymers with lower acid can be prepared.

Specific acid-copolymers include ethylene/(meth)acrylic acid/n-butyl(meth)acrylate, ethylene/(meth)acrylic acid/iso-butyl(meth)acrylate, ethylene/(meth)acrylic acid/methyl(meth)acrylate, and ethylene/(meth)acrylic acid/ethyl(meth)acrylate terpolymers.

The organic acids employed are aliphatic, mono-functional (saturated, unsaturated, or is multi-unsaturated) organic acids, particularly those having fewer than 36 carbon atoms. Also salts of these organic acids may be employed. Fatty acids or fatty acid salts are preferred. The salts may be any of a wide variety, particularly including the barium, lithium, sodium, zinc, bismuth, potassium, strontium, magnesium or calcium salts of the organic acids. Particular organic acids useful in the present invention include caproic acid, caprylic acid, capric acid, lauric acid, stearic acid, behenic acid, erucic acid, oleic acid, and linoleic acid.

The optional filler component is chosen to impart additional density to blends of the previously described compo-

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nents, the selection being dependent upon the different parts (e.g., cover, mantle, core, center, intermediate layers in a multilayered core or ball) and the type of golf ball desired (e.g., one-piece, two-piece, three-piece or multiple-piece ball), as will be more fully detailed below.

Generally, the filler will be inorganic having a density greater than about 4 g/cm³, preferably greater than 5 g/cm³, and will be present in amounts between 0 to about 60 wt. % based on the total weight of the composition. Examples of useful fillers include zinc oxide, barium sulfate, lead silicate and tungsten carbide, as well as the other well-known fillers used in golf balls. It is preferred that the filler materials be non-reactive or almost non-reactive and not stiffen or raise the compression nor reduce the coefficient of restitution significantly.

Additional optional additives useful in the practice of the subject invention include acid copolymer wax (e.g., Allied wax AC 143 believed to be an ethylene/16-18% acrylic acid copolymer with a number average molecular weight of 2,040), which assist in preventing reaction between the filler materials (e.g., ZnO) and the acid moiety in the ethylene copolymer. Other optional additives include TiO₂, which is used as a whitening agent; optical brighteners; surfactants; processing aids; etc.

Ionomers may be blended with conventional ionomeric copolymers (di-, ter-, etc.), using well-known techniques, to manipulate product properties as desired. The blends would still exhibit lower hardness and higher resilience when compared with blends based on conventional ionomers.

Also, ionomers can be blended with non-ionic thermoplastic resins to manipulate product properties. The non-ionic thermoplastic resins would, by way of non-limiting illustrative examples, include thermoplastic elastomers, such as polyurethane, poly-ether-ester, poly-amide-ether, polyether-urea, PEBAX® (a family of block copolymers based on poly-ether-block-amide, commercially supplied by Atochem), styrene-butadiene-styrene (SBS) block copolymers, styrene (ethylene-butylene)-styrene block copolymers, etc., poly amide (oligomeric and polymeric), polyesters, polyolefins including PE, PP, E/P copolymers, etc., ethylene copolymers with various comonomers, such as vinyl acetate, (meth)acrylates, (meth)acrylic acid, epoxy-functionalized monomer, CO, etc., functionalized polymers with maleic anhydride grafting, epoxidization etc., elastomers, such as EPDM, metallocene catalyzed PE and copolymer, ground up powders of the thermoset elastomers, etc. Such thermoplastic blends comprise about 1% to about 99% by weight of a first thermoplastic and about 99% to about 1% by weight of a second thermoplastic.

Additionally, the compositions of U.S. Pat. Nos. 6,953,820 and 6,653,382, both of which are incorporated herein in their entirety, discuss compositions having high COR when formed into solid spheres.

The thermoplastic composition of this invention comprises a polymer which, when formed into a sphere that is 1.50 to 1.54 inches in diameter, has a coefficient of restitution when measured by firing the sphere at an initial velocity of 125 ft/s against a steel plate positioned 3 ft from the point where initial velocity and rebound velocity are determined and by dividing the rebound velocity from the plate by the initial velocity and an Atti compression of no more than 100.

Initial velocity of a golf ball after impact with a golf club is governed by the United States Golf Association ("USGA"). The USGA requires that a regulation golf ball can have an initial velocity of no more than 250 ft/s \pm 2% (effectively 255 ft/s). The USGA initial velocity limit is related to the ultimate distance that a golf ball may travel (280 yards \pm 6%), and is

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also related to the COR. The COR is the ratio of the a) relative velocity between two objects after direct impact to the b) relative velocity before impact. As a result, the COR can vary from 0 to 1.0, with 1.0 being equivalent to a perfectly or completely elastic collision and 0 being equivalent to a perfectly plastic or completely inelastic collision.

One conventional technique for measuring COR uses a golf ball or sphere, an air cannon, and a stationary steel plate. The steel plate provides an impact surface weighing about 100 lb (45 kg). A pair of ballistic light screens, which measure ball velocity, are spaced apart and located between the air cannon and the steel plate. The golf ball is fired from the air cannon toward the steel plate over a range of test velocities from 50 ft/s to 180 ft/s. As the ball travels toward the steel plate, it activates each light screen so that the time at each light screen is measured. This provides an incoming time period proportional to the ball incoming velocity. The ball impacts the steel plate and rebounds through the light screens, which again measure the time period required to transit between the light screens. This provides an outgoing transit time period proportional to the ball outgoing velocity. The COR can be calculated by the ratio of the outgoing transit time period to the incoming transit time period, $COR = T_{out}/T_{in}$.

Another COR measuring method uses a titanium disk. The titanium disk, intending to simulate a golf club, is circular and has a diameter of about 4 inches and has a mass of about 200 g. The impact face of the titanium disk may also be flexible and has its own COR, as discussed further below. The disk is mounted on an X—Y—Z table so that its position can be adjusted relative to the launching device prior to testing. A pair of ballistic light screens are spaced apart and located between the launching device and the titanium disk. The ball is fired from the launching device toward the titanium disk at a predetermined test velocity. As the ball travels toward the titanium disk, it activates each light screen so that the time period to transit between the light screens is measured. This provides an incoming transit time period proportional to the ball incoming velocity. The ball impacts the titanium disk, and rebounds through the light screens which measure the time period to transit between the light screens. This provides an outgoing transit time period proportional to the ball's outgoing velocity. Coefficient of restitution can be calculated from the ratio of the outgoing time period to the incoming time period along with the mass of the disk and ball: $COR = [(T_{out}/T_{in})(M_e + M_b) + M_b]/M_e$.

The thermoplastic composition of this invention preferably comprises (a) aliphatic, mono-functional organic acid(s) having fewer than 36 carbon atoms; and (b) ethylene, C_3 to C_8 α,β -ethylenically unsaturated carboxylic acid copolymer(s) and ionomer(s) thereof, wherein greater than 90%, preferably near 100%, and more preferably 100% of all the acid of (a) and (b) are neutralized.

The thermoplastic composition preferably comprises melt-processible, highly-neutralized (greater than 90%, preferably near 100%, and more preferably 100%) polymer of (1) ethylene, C_3 to C_8 α,β -ethylenically unsaturated carboxylic acid copolymers that have their crystallinity disrupted by addition of a softening monomer or other means such as high acid levels, and (2) non-volatile, non-migratory agents such as organic acids (or salts) selected for their ability to substantially or totally suppress any remaining ethylene crystallinity. Agents other than organic acids (or salts) may be used.

It has been found that, by modifying an acid copolymer or ionomer with a sufficient amount of specific organic acids (or salts thereof); it is possible to highly neutralize the acid copolymer without losing processibility or properties such as elongation and toughness. The organic acids employed in the

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present invention are aliphatic, mono-functional, saturated or unsaturated organic acids, particularly those having fewer than 36 carbon atoms, and particularly those that are non-volatile and non-migratory and exhibit ionic array plasticizing and ethylene crystallinity suppression properties.

With the addition of sufficient organic acid, greater than 90%, nearly 100%, and preferably 100% of the acid moieties in the acid copolymer from which the ionomer is made can be neutralized without losing the processibility and properties of elongation and toughness.

The melt-processible, highly-neutralized acid copolymer ionomer can be produced by the following:

(a) melt-blending (1) ethylene α,β -ethylenically unsaturated C_{3-8} carboxylic acid copolymer(s) or melt-processible ionomer(s) thereof (ionomers that are not neutralized to the level that they have become intractable, that is not melt-processible) with (1) one or more aliphatic, mono-functional, saturated or unsaturated organic acids having fewer than 36 carbon atoms or salts of the organic acids, and then concurrently or subsequently.

(b) adding a sufficient amount of a cation source to increase the level of neutralization all the acid moieties (including those in the acid copolymer and in the organic acid) to greater than 90%, preferably near 100%, more preferably to 100%.

Preferably, highly-neutralized thermoplastics of the invention can be made by:

(a) melt-blending (1) ethylene, α,β -ethylenically unsaturated C_{3-8} carboxylic acid copolymer(s) or melt-processible ionomer(s) thereof that have their crystallinity disrupted by addition of a softening monomer or other means with (2) sufficient non-volatile, non-migratory agents to substantially remove the remaining ethylene crystallinity, and then concurrently or subsequently.

(b) adding a sufficient amount of a cation source to increase the level of neutralization all the acid moieties (including those in the acid copolymer and in the organic acid if the non-volatile, non-migratory agent is an organic acid) to greater than 90%, preferably near 100%, more preferably to 100%.

The acid copolymers used in the present invention to make the ionomers are preferably 'direct' acid copolymers. They are preferably alpha olefin, particularly ethylene, C_{3-8} α,β -ethylenically unsaturated carboxylic acid, particularly acrylic and methacrylic acid, copolymers. They may optionally contain a third softening monomer. By "softening," it is meant that the crystallinity is disrupted (the polymer is made less crystalline). Suitable "softening" comonomers are monomers selected from alkyl acrylate, and alkyl methacrylate, wherein the alkyl groups have from 1-8 carbon atoms.

The acid copolymers, when the alpha olefin is ethylene, can be described as E/X/Y copolymers where E is ethylene, X is the α,β -ethylenically unsaturated carboxylic acid, and Y is a softening comonomer. X is preferably present in 3-30 (preferably 4-25, most preferably 5-20) wt. % of the polymer, and Y is preferably present in 0-30 (alternatively 3-25 or 10-23) wt. % of the polymer.

In one embodiment, golf balls made with the cores of the invention enjoy high COR at relatively low club speeds. The COR of these balls is higher than the COR of similar balls with higher compression cores at relatively low club speeds. At higher club speeds, however, the COR of golf balls with low compression cores can be lower than the COR of balls with higher compression cores. As illustrated herein, a first golf ball with a 1.505-inch diameter core and a core compression of 48 (hereinafter "Sample-48") and a second golf ball with a 1.515-inch diameter core and a core compression of 80 (hereinafter "Sample-80") were subject to the following dis-

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tance and COR tests. Sample-48 and Sample-80 have essentially the same size core and similar dual-layer cover. The single most significant difference between these two balls is the compression of the respective cores.

As used in the ball speed test, the “average driver set-up” refers to a set of launch conditions, i.e., at a club head speed to which a mechanical golf club has been adjusted so as to generate a ball speed of about 140 ft/s. Similarly, the “standard driver set-up” refers to a similar ball speed at launch conditions of about 160 ft/s; the “Pro 167 set-up” refers to a ball speed at launch conditions of about 167 ft/s; and the “Big Pro 175 set-up” refers to a ball speed at launch conditions of about 175 ft/s. Also, as used in the COR test, the mass plate is a 45-kg plate (100 lb) against which the balls strike at the indicated speed. The 200-g solid plate is a smaller mass that the balls strike and resembles the mass of a club head. The 199.8-g calibration plate resembles a driver with a flexible face that has a COR of 0.830.

The ball speed test results show that while Sample-48 holds a ball speed advantage at club speeds of 140 ft/s to 160 ft/s launch conditions, Sample-80 decidedly has better ball speed at 167 ft/s and 175 ft/s launch conditions.

Similarly, the COR test results show that at the higher collision speed (160 ft/s), the COR generally goes down for both balls, but the 199.8-g calibration test shows that the COR of the higher compression Sample-80 is significantly better than the lower compression Sample-48 at the collision speed (160 ft/s). Additionally, while the COR generally goes down for both balls, the rate of decrease is much less for Sample-80 than for Sample-48. Unless specifically noted, COR values used hereafter are measured by either the mass plate method or the 200-gram solid plate method, i.e., where the impact plate is not flexible. Unless otherwise noted, COR values used hereafter are measured by either the mass plate method or the 200-g solid plate method.

Without being limited to any particular theory, the inventors of the present invention believe that at high impact, the ball with lower core compression deforms more than the ball with higher core compression. Such deformation negatively affects the initial velocity and COR of the ball.

In accordance to the present invention, a golf ball is provided with a low compression and high COR layer, which is supported or otherwise reinforced by a low deformation layer.

On the other hand, the low deformation layer in accordance to the present invention may comprise a durable, low deformation material such as metal, rigid plastics, or polymers re-enforced with high strength organic or inorganic fillers or fibers, or blends or composites thereof, as discussed below. Suitable plastics or polymers include, but not limited to, high cis- or trans-polybutadiene, one or more of partially or fully neutralized ionomers including those neutralized by a metal ion source wherein the metal ion is the salt of an organic acid, polyolefins including polyethylene, polypropylene, polybutylene and copolymers thereof including polyethylene acrylic acid or methacrylic acid copolymers, or a terpolymer of ethylene, a softening acrylate class ester such as methyl acrylate, n-butyl-acrylate or iso-butyl-acrylate, and a carboxylic acid such as acrylic acid or methacrylic acid (e.g., terpolymers including polyethylene-methacrylic acid-n or iso-butyl acrylate and polyethylene-acrylic acid-methyl acrylate, polyethylene ethyl or methyl acrylate, polyethylene vinyl acetate, polyethylene glycidyl alkyl acrylates). Suitable polymers also include metallocene catalyzed polyolefins, polyesters, polyamides, non-ionomeric thermoplastic elastomers, copolyether-esters, copolyether-amides, EPR, EPDM, thermoplastic or thermosetting polyurethanes, polyureas, polyurethane ionomers, epoxies, polycarbonates, polybutadiene,

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polyisoprene, and blends thereof. In the case of metallocenes, the polymer may be cross-linked with a free radical source, such as peroxide, or by high radiation.

Spheres were prepared using fully neutralized ionomers A and B.

TABLE I

Sample	Resin Type (%)	Acid Type (%)	Cation (% neut*)	M.I. (g/10 min)
1A	A (60)	Oleic (40)	Mg (100)	1.0
2B	A (60)	Oleic (40)	Mg (105)*	0.9
3C	B (60)	Oleic (40)	Mg (100)	0.9
4D	B (60)	Oleic (40)	Mg (105)*	0.9
5E	B (60)	Stearic (40)	Mg (100)	0.85

A - 76.9% ethylene, 14.8% normal butyl acrylate, 8.3% acrylic acid

B - 75% ethylene, 14.9% normal butyl acrylate, 10.1% acrylic acid

*indicates that cation was sufficient to neutralize 105% of all the acid in the resin and the organic acid.

These compositions were molded into 1.53-inch spheres for which data is presented in the following table.

TABLE II

Sample	Atti Compression	COR @ 125 ft/s
1A	75	0.826
2B	75	0.826
3C	78	0.837
4D	76	0.837
5E	97	0.807

Further testing of commercially available highly neutralized polymers HNP1 and HNP2 had the following properties.

TABLE III

Material Properties		
	HNP1	HNP2
Specific Gravity (g/cm ³)	0.966	0.974
Melt Flow, 190° C., 10-kg load	0.65	1.0
Shore D Flex Bar (40 hr)	47.0	46.0
Shore D Flex Bar (2 week)	51.0	48.0
Flex Modulus, psi (40 hr)	25,800	16,100
Flex Modulus, psi (2 week)	39,900	21,000
DSC Melting Point (° C.)	61.0	61/101
Moisture (ppm)	1500	4500
Weight % Mg	2.65	2.96

TABLE IV

Solid Sphere Data					
Material	HNP1	HNP2	HNP2a	HNP1a	HNP1a/HNP2a (50:50 blend)
Spec. Grav. (g/cm ³)	0.954	0.959	1.153	1.146	1.148
Filler	None	None	Tungsten	Tungsten	Tungsten
Compression	107	83	86	62	72
COR	0.827	0.853	0.844	0.806	0.822
Shore D	51	47	49	42	45
Shore C			79	72	75

These materials are exemplary examples of the preferred center and/or core layer compositions of the present invention. They may also be used as a cover layer herein.

The golf ball components of the present invention, in particular the core (center and/or outer core layers) may be formed from a co-polymer of ethylene and an α,β -unsatur-

ated carboxylic acid. In another embodiment, they may be formed from a terpolymer of ethylene, an α,β -unsaturated carboxylic acid, and an n-alkyl acrylate. Preferably, the α,β -unsaturated carboxylic acid is acrylic acid or methacrylic acid. In a preferred embodiment, the n-alkyl acrylate is n-butyl acrylate. Further, in a preferred form, the co- or terpolymer comprises a level of fatty acid salt greater than 5 phr of the base resin. The preferred fatty acid salt is magnesium oleate or magnesium stearate.

It is highly preferred that the carboxylic acid in the intermediate layer is 100% neutralized with metal ions. The metal ions used to neutralize the carboxylic acid may be any metal ion known in the art. Preferably, the metal ions comprise magnesium ions. If the material used in the intermediate layer is not 100% neutralized, the resultant resilience properties such as COR and initial velocity may not be sufficient to produce the improved initial velocity and distance properties of the present invention.

The golf ball components can comprise various levels of the three components of the co- or terpolymer as follows: from about 60 to about 90% ethylene, from about 8 to about 20% by weight of the α,β -unsaturated carboxylic acid, and from 0% to about 25% of the n-alkyl acrylate. The co- or terpolymer may also contain an amount of a fatty acid salt. The fatty acid salt preferably comprises magnesium oleate. These materials are commercially available from DuPont, under the tradename DuPont HPF®.

In one embodiment, the core and/or core layers (or other intermediate layers) comprises a copolymer of about 81% by weight ethylene and about 19% by weight acrylic acid, wherein 100% of the carboxylic acid groups are neutralized with magnesium ions. The copolymer also contains at least 5 phr of magnesium oleate. Material suitable for use as this layer is available from DuPont under the tradename DuPont HPF SEP 1313-4®.

In a second preferred embodiment, the core and/or core layers (or other intermediate layers) comprise a copolymer of about 85% by weight ethylene and about 15% by weight acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. The copolymer also contains at least 5 phr of magnesium oleate. Material suitable for use as this layer is available from DuPont under the tradename DuPont HPF SEP 1313-3®.

In a third preferred embodiment, the core and/or core layers (or other intermediate layers) comprise a copolymer of about 88% by weight ethylene and about 12% by weight acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. The copolymer also contains at least 5 phr of magnesium oleate. Material suitable for use as this layer is available from DuPont under the tradename DuPont HPF AD1027®.

In a further preferred embodiment, the core and/or core layers (or other intermediate layers) are adjusted to a target specific gravity to enable the ball to be balanced. For a 1.68-inch diameter golf ball having a ball weight of about 1.61 oz, the target specific gravity is about 1.125. It will be appreciated by one of ordinary skill in the art that the target specific gravity will vary based upon the size and weight of the golf ball. The specific gravity is adjusted to the desired target through the use of inorganic fillers. Preferred fillers used for compounding the inner layer to the desired specific gravity include, but are not limited to, tungsten, zinc oxide, barium sulfate and titanium dioxide. Other suitable fillers, in particular nano or hybrid materials, include those described in U.S. Pat. No. 6,793,592 and U.S. application Ser. No. 10/037,987, which are incorporated herein, in their entirety, by reference thereto.

Some preferred golf ball layers formed from the above compositions were molded onto a golf ball center using DuPont HPF RX-85®, Dupont HPF SEP 1313-3®, or DuPont HPF SEP 1313-4®. 1) DuPont HPF RX-85®, a copolymer of about 88% ethylene and about 12% acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the copolymer contains a fixed amount of magnesium oleate. This material was compounded to a specific gravity of about 1.125 using tungsten. The Shore D hardness of this material (as measured on the curved surface of the inner cover layer) was about 58 to about 60. 2) DuPont HPF SEP 1313-3®, a copolymer of about 85% ethylene and about 15% acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the copolymer contains a fixed amount of magnesium oleate. This material was compounded to a specific gravity of about 1.125 using tungsten. The Shore D hardness of this material (as measured on the curved surface of the inner cover layer) was about 58-60. 3) DuPont HPF SEP 1313-4®, a copolymer of about 81% ethylene and about 19% acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the copolymer contains a fixed amount of magnesium oleate. This material was compounded to a specific gravity of about 1.125 using tungsten. The Shore D hardness of this material (as measured on the curved surface of the inner cover layer) was about 58-60.

The centers/cores/layers can also comprise various levels of the three components of the terpolymer as follows: from about 60% to 80% ethylene; from about 8% to 20% by weight of the α,β -unsaturated carboxylic acid; and from about 0% to 25% of the n-alkyl acrylate, preferably 5% to 25%. The terpolymer will also contain an amount of a fatty acid salt, preferably magnesium oleate. These materials are commercially available under the trade name DuPont® HPF™. In a preferred embodiment, a terpolymer suitable for the invention will comprise from about 75% to 80% by weight ethylene, from about 8% to 12% by weight of acrylic acid, and from about 8% to 17% by weight of n-butyl acrylate, wherein all of the carboxylic acid is neutralized with magnesium ions, and comprises at least 5 phr of magnesium oleate.

In another preferred embodiment, the cover layer will comprise a terpolymer of about 70% to 75% by weight ethylene, about 10.5% by weight acrylic acid, and about 15.5% to 16.5% by weight n-butyl acrylate. The acrylic acid groups are 100% neutralized with magnesium ions. The terpolymer will also contain an amount of magnesium oleate. Materials suitable for use as this layer are sold under the trade name DuPont® HPF™ AD 1027.

In yet another preferred embodiment, the centers/cores/layers comprise a copolymer comprising about 88% by weight of ethylene and about 12% by weight acrylic acid, with 100% of the acrylic acid neutralized by magnesium ions. The centers/cores/layers may also contain magnesium oleate. Material suitable for this embodiment was produced by DuPont as experimental product number SEP 1264-3. Preferably the centers/cores/layers are adjusted to a target specific gravity of 1.125 using inert fillers to adjust the density with minimal effect on the performance properties of the cover layer. Preferred fillers used for compounding the centers/cores/layers to the desired specific gravity include but are not limited to tungsten, zinc oxide, barium sulfate, and titanium dioxide.

A first set of intermediate layers were molded onto cores using DuPont® HPF™ AD1027, which is a terpolymer of about 73% to 74% ethylene, about 10.5% acrylic acid, and about 15.5% to 16.5% n-butyl acrylate, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the

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terpolymer contains a fixed amount of greater than 5 phr magnesium oleate. This material is compounded to a specific gravity of about 1.125 using barium sulfate and titanium dioxide. The Shore D hardness of this material (as measured on the curved surface of the inner cover layer) is about 58-60.

A second set of layers were molded onto each of the experimental cores using DuPont experimental HPF™ SEP 1264-3, which is a copolymer of about 88% ethylene and about 12% acrylic acid, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the copolymer contains a fixed amount of at least 5 phr magnesium oleate. This material is compounded to a specific gravity of about 1.125 using zinc oxide. The Shore D hardness of this material (as measured on the curved surface of the inner cover layer) is about 61-64.

A first set of covers were molded onto each of the core/layer components using DuPont HPF™ 1000, which is a terpolymer of about 75% to 76% ethylene, about 8.5% acrylic acid, and about 15.5% to 16.5% n-butyl acrylate, wherein 100% of the acid groups are neutralized with magnesium ions. Further, the terpolymer contains a fixed amount of at least 5 phr of magnesium stearate. This material is compounded to a target specific gravity of about 1.125 using barium sulfate and titanium dioxide. The Shore D hardness of this material (as measured on the curved surface of the molded golf ball) is about 60-62.

In one embodiment, the formation of a golf ball starts with forming the inner core. The inner core, outer core, and the cover are formed by compression molding, by injection molding, or by casting. These methods of forming cores and covers of this type are well known in the art. The materials used for the inner and outer core, as well as the cover, are selected so that the desired playing characteristics of the ball are achieved. The inner and outer core materials have substantially different material properties so that there is a predetermined relationship between the inner and outer core materials, to achieve the desired playing characteristics of the ball.

In one embodiment, the inner core is formed of a first material having a first Shore D hardness, a first elastic modulus, a first specific gravity, and a first Bashore resilience. The outer core is formed of a second material having a second Shore D hardness, a second elastic modulus, a second specific gravity, and a second Bashore resilience. Preferably, the material property of the first material equals at least one selected from the group consisting of the first Shore D hardness differing from the second Shore D hardness by at least 10 points, the first elastic modulus differing from the second elastic modulus by at least 10%, the first specific gravity differing from the second specific gravity by at least 0.1, or a first Bashore resilience differing from the second Bashore resilience by at least 10%. It is more preferred that the first material have all of these material property relationships.

Moreover, it is preferred that the first material has the first Shore D hardness between about 30 and about 80, the first elastic modulus between about 5,000 psi and about 100,000 psi, the first specific gravity between about 0.8 and about 1.6, and the first Bashore resilience greater than 30%.

In another embodiment, the first Shore D hardness is less than the second Shore D hardness, the first elastic modulus is less than the second elastic modulus, the first specific gravity is less than the second specific gravity, and the first Bashore resilience is less than the second Bashore resilience. In another embodiment, the first material properties are greater than the second material properties. The relationship between the first and second material properties depends on the desired playability characteristics.

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Suitable inner and outer core materials include HNP's neutralized with organic fatty acids and salts thereof, metal cations, or a combination of both, thermosets, such as rubber, polybutadiene, polyisoprene; thermoplastics, such as ionomer resins, polyamides or polyesters; or thermoplastic elastomers. Suitable thermoplastic elastomers include PEBAX®, HYTREL®, thermoplastic urethane, and KRATON®, which are commercially available from Elf-Atochem, DuPont, BF Goodrich, and Shell, respectively. The inner and outer core materials can also be formed from a castable material. Suitable castable materials include, but are not limited to, urethane, urea, epoxy, diols, or curatives.

The cover is selected from conventional materials used as golf ball covers based on the desired performance characteristics. The cover may be comprised of one or more layers. Cover materials such as ionomer resins, blends of ionomer resins, thermoplastic or thermoset urethanes, and balata, can be used as known in the art and discussed above. In other embodiments, additional layers may be added to those mentioned above or the existing layers may be formed by multiple materials.

When the core is formed with a fluid-filled center, the center is formed first then the inner core is molded around the center. Conventional molding techniques can be used for this operation. Then the outer core and cover are formed thereon, as discussed above. The fluid within the inner core can be a wide variety of materials including air, water solutions, liquids, gels, foams, hot-melts, other fluid materials and combinations thereof. The fluid is varied to modify the performance parameters of the ball, such as the moment of inertia or the spin decay rate. Examples of suitable liquids include either solutions such as salt in water, corn syrup, salt in water and corn syrup, glycol and water or oils. The liquid can further include pastes, colloidal suspensions, such as clay, barytes, carbon black in water or other liquid, or salt in water/glycol mixtures. Examples of suitable gels include water gelatin gels, hydrogels, water/methyl cellulose gels and gels comprised of copolymer rubber based materials such as styrene-butadiene-styrene rubber and paraffinic and/or naphthenic oil. Examples of suitable melts include waxes and hot melts. Hot-melts are materials which at or about normal room temperatures are solid but at elevated temperatures become liquid. A high melting temperature is desirable since the liquid core is heated to high temperatures during the molding of the inner core, outer core, and the cover. The liquid can be a reactive liquid system, which combines to form a solid. Examples of suitable reactive liquids are silicate gels, agar gels, peroxide cured polyester resins, two part epoxy resin systems and peroxide cured liquid polybutadiene rubber compositions.

The "effective compression constant," which is designated EC, is the ratio of deflection of a 1.50 inch diameter sphere made of any single material used in the core under a 100 kg load that as represented by the formula $EC = F/d$, where, F is a 100 kg load; and d is the deflection in millimeters. If the sphere tested is only inner core material, the effective compression constant for the inner core material alone is designated EC_{IC} . If the sphere tested is only outer core material, the effective compression constant for the outer core material alone is designated EC_{OC} . The sum of the constants for the inner core EC_{IC} and outer core EC_{OC} is the constant EC_S . If the sphere tested is inner and outer core material, the core effective compression constant is designated EC_C . It has been determined that very favorable cores are formed when their core effective compression constant EC_C is less than the sum of the effective compression constants of the inner core and outer core EC_S . It is recommended that the core effective

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compression constant EC_C is less than about 90% of the sum of the effective compression constants of the inner core and outer core EC_S . More preferably, the core effective compression constant EC_C is less than or equal to about 50% of the sum of the effective compression constants of the inner core and outer core EC_S . The ratios of the inner core material to outer core material and the geometry of the inner core to the outer core are selected to achieve these core effective compression constants.

The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball cured polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D.

In addition to the HNP's neutralized with organic fatty acids and salts thereof, core compositions may comprise at least one rubber material having a resilience index of at least about 40. Preferably the resilience index is at least about 50. Polymers that produce resilient golf balls and, therefore, are suitable for the present invention, include but are not limited to CB23, CB22, commercially available from Bayer Corp. of Orange, Tex., BR60, commercially available from Enichem of Italy, and 1207G, commercially available from Goodyear Corp. of Akron, Ohio.

Additionally, the unvulcanized rubber, such as polybutadiene, in golf balls prepared according to the invention typically has a Mooney viscosity of between about 40 and about 80, more preferably, between about 45 and about 65, and most preferably, between about 45 and about 55. Mooney viscosity is typically measured according to ASTM-D1646.

When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 500 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-D2240, less than about 45 Shore D, preferably less than about 40 Shore D, more preferably between about 25 and about 40 Shore D, and most preferably between about 30 and about 40 Shore D. The casing preferably has a material hardness of less than about 70 Shore D, more preferably between about 30 and about 70 Shore D, and most preferably, between about 50 and about 65 Shore D.

In a preferred embodiment, the intermediate layer material hardness is between about 40 and about 70 Shore D and the outer cover layer material hardness is less than about 40 Shore D. In a more preferred embodiment, a ratio of the intermediate layer material hardness to the outer cover layer material hardness is greater than 1.5.

It should be understood, especially to one of ordinary skill in the art, that there is a fundamental difference between "material hardness" and "hardness, as measured directly on a golf ball." Material hardness is defined by the procedure set forth in ASTM-D2240 and generally involves measuring the hardness of a flat "slab" or "button" formed of the material of which the hardness is to be measured. Hardness, when measured directly on a golf ball (or other spherical surface) is a completely different measurement and, therefore, results in a

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different hardness value. This difference results from a number of factors including, but not limited to, ball construction (i.e., core type, number of core and/or cover layers, etc.), ball (or sphere) diameter, and the material composition of adjacent layers. It should also be understood that the two measurement techniques are not linearly related and, therefore, one hardness value cannot easily be correlated to the other.

In one embodiment, the core of the present invention has an Atti compression of between about 50 and about 90, more preferably, between about 60 and about 85, and most preferably, between about 65 and about 85. The overall outer diameter ("OD") of the core is less than about 1.590 inches, preferably, no greater than 1.580 inches, more preferably between about 1.540 inches and about 1.580 inches, and most preferably between about 1.525 inches to about 1.570 inches. The OD of the casing of the golf balls of the present invention is preferably between 1.580 inches and about 1.640 inches, more preferably between about 1.590 inches to about 1.630 inches, and most preferably between about 1.600 inches to about 1.630 inches.

Additionally, the core may be a two- or three-piece core, wherein the outermost core layer is formed from an HNP composition. In a two-piece core embodiment, the center or innermost core layer has a diameter of about 1.00 inches to about 1.60 inches, preferably about 1.20 inches to about 1.58 inches, more preferably about 1.30 inches to about 1.56 inches, and most preferably about 1.40 inches to about 1.55 inches. The outermost core layer (comprising the HNP composition) typically has a thickness of about 0.010 inches to about 0.250 inches, preferably about 0.020 inches to about 0.150 inches, more preferably about 0.040 inches to about 0.125 inches, and most preferably about 0.050 inches to about 0.095 inches.

In a three-piece core embodiment, the center or innermost core layer has a diameter of about 0.25 inches to about 1.50 inches, preferably about 0.50 inches to about 1.40 inches, more preferably about 0.75 inches to about 1.30 inches, and most preferably about 1.0 inches to about 1.20 inches. The intermediate core layer (between the innermost core layer (or center) and the outer core layer) typically has a thickness of about 0.050 inches to about 0.550 inches, preferably about 0.100 inches to about 0.300 inches, more preferably about 0.125 inches to about 0.290 inches, and most preferably about 0.200 inches to about 0.275 inches. The outermost core layer (comprising HNP) typically has a thickness of about 0.010 inches to about 0.250 inches, preferably about 0.020 inches to about 0.150 inches, more preferably about 0.040 inches to about 0.125 inches, and most preferably about 0.050 inches to about 0.095 inches.

In a preferred embodiment, the innermost core (center) has an outer surface hardness that is at least 5 Shore C less than the hardness of both the inner and outer surfaces of the outer core layer, preferably at least 7 Shore C less, most preferably at least 9 Shore C less.

The inner core surface hardness typically ranges from about 50 Shore C to about 96 Shore C; preferably about 57 Shore C to about 89 Shore C; more preferably about 63 Shore C to about 82 Shore C; most preferably about 63 Shore C, 67 Shore C, 71 Shore C, 75 Shore C, or 79 Shore C. The outer core surface hardness typically ranges from about 57 Shore C to about 100 Shore C; preferably about 63 Shore C to about 96 Shore C; more preferably about 70 Shore C to about 89 Shore C; and most preferably about 70 Shore C, 74 Shore C, 81 Shore C, 82 Shore C, or 86 Shore C.

In a preferred embodiment, the innermost core (center) has an outer surface hardness that is at least 3 Shore D less than

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the hardness of both the inner and outer surfaces of the outer core layer, preferably at least 5 Shore D less, more preferably at least 7 Shore D less.

The inner core surface hardness typically ranges from about 30 Shore D to about 65 Shore D; preferably about 35 Shore D to about 60 Shore D; more preferably about 40 Shore D to about 55 Shore D; most preferably about 40 Shore D, 43 Shore D, 46 Shore D, 49 Shore D, or 52 Shore D. The outer core surface hardness typically ranges from about 35 Shore D to about 70 Shore D; preferably about 40 Shore D to about 65 Shore D; more preferably about 45 Shore D to about 60 Shore D; and most preferably about 45 Shore D, 48 Shore D, 51 Shore D, 54 Shore D, or 57 Shore D.

The present multilayer golf ball can have an overall diameter of any size. Although the USGA specifications limit the minimum size of a competition golf ball to 1.680 inches. There is no specification as to the maximum diameter. Golf balls of any size, however, can be used for recreational play. The preferred diameter of the present golf balls is from about 1.680 inches to about 1.800 inches. The more preferred diameter is from about 1.680 inches to about 1.760 inches. The most preferred diameter is about 1.680 inches to about 1.740 inches.

The golf balls of the present invention should have a moment of inertia ("MOI") of less than about 85 and, preferably, less than about 83. The MOI is typically measured on model number MOI-005-104 MOI Instrument manufactured by Inertia Dynamics of Collinsville, Conn. The instrument is plugged into a PC for communication via a COMM port and is driven by MOI Instrument Software version #1.2. U.S. Pat. Nos. 6,193,619; 6,207,784; 6,221,960; 6,414,082; 6,476,130; and 6,287,638 are incorporated in their entirety herein by express reference thereto. The highly-neutralized polymers of the present invention may also be used in golf equipment, in particular, inserts for golf clubs, such as putters, irons, and woods, and in golf shoes and components thereof.

As used herein, the term "about," used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range. Other than in the operating examples, or unless otherwise expressly specified, all of the numerical ranges, amounts, values and percentages such as those for amounts of materials, and others in the specification may be read as if prefaced by the word "about" even though the "about" may not expressly appear with the value, amount or range. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Furthermore, when numerical ranges of varying scope are set forth herein, it is contemplated that any combination of these values inclusive of the recited values may be used. The invention described and claimed herein is not to be limited in scope by the specific embodiments

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herein disclosed, since these embodiments are intended solely as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball comprising:

an inner core layer comprising a thermoset rubber composition and having a surface hardness;
a thermoplastic outer core layer having a surface hardness, an inner surface hardness, and comprising a copolymer of ethylene and an α,β -unsaturated carboxylic acid, an organic acid or salt thereof, and sufficient cation source to fully-neutralize the acid groups of the copolymer;
an inner cover layer; and
an outer cover layer;

wherein the surface hardness of the inner core is less than the surface hardness of the outer core layer by 3 Shore D or greater and less than the inner surface hardness of the outer core layer by 3 Shore D or greater.

2. The golf ball of claim 1, wherein the surface hardness of the inner core is less than the surface hardness of the outer core layer by 5 Shore D or greater and less than the inner surface hardness of the outer core layer by 5 Shore D or greater.

3. The golf ball of claim 2, wherein the surface hardness of the inner core is less than the surface hardness of the outer core layer by 7 Shore D or greater and less than the inner surface hardness of the outer core layer by 7 Shore D or greater.

4. The golf ball of claim 1, wherein the cation source is selected from a group consisting of metal cations of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, and aluminum.

5. The golf ball of claim 1, wherein the organic acid salt comprises an organic acid selected from the group consisting of aliphatic organic acids, aromatic organic acids, saturated mono- or multi-functional organic acids, unsaturated mono- or multi-functional organic acids, and multi-unsaturated mono- or multi-functional organic acids.

6. The golf ball of claim 1, wherein the organic acid comprises stearic acid, behenic acid, erucic acid, oleic acid, linoleic acid or dimerized derivatives thereof.

7. The golf ball of claim 1, wherein the organic acid salt comprises a cation selected from the group consisting of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, and calcium.

8. The golf ball of claim 1, wherein the outer cover is a castable polyurea or polyurethane.

9. The golf ball of claim 1, wherein the inner cover layer comprises a polyurethane, a polyurea, a polyurethane-urea hybrid, a polyurea-urethane hybrid, or an ionomer.

10. The golf ball of claim 1, wherein the inner core has a diameter of 0.8 inches to 1.4 inches.

11. The golf ball of claim 1, wherein the thermoplastic outer core layer has a thickness of 0.040 inches or greater.

12. The golf ball of claim 11, wherein the thermoplastic outer core layer has a thickness of 0.090 inches to 0.180 inches.

* * * * *

Exhibit E

(12) **United States Patent**
Sullivan et al.

(10) **Patent No.:** **US 8,444,507 B2**
(45) **Date of Patent:** ***May 21, 2013**

(54) **MULTI-LAYER GOLF BALL**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.
This patent is subject to a terminal disclaimer.

(21) Appl. No.: **13/397,906**

(22) Filed: **Feb. 16, 2012**

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Related U.S. Application Data

(63) Continuation of application No. 13/024,901, filed on Feb. 10, 2011, now Pat. No. 8,123,632, which is a continuation of application No. 12/233,776, filed on Sep. 19, 2008, now Pat. No. 7,887,437, which is a continuation-in-part of application No. 12/048,003, filed on Mar. 13, 2008, now abandoned, which is a continuation-in-part of application No. 11/767,070, filed on Jun. 22, 2007, now abandoned, which is a continuation-in-part of application No. 10/773,906, filed on Feb. 6, 2004, now Pat. No. 7,255,656, which is a continuation-in-part of application No. 10/341,574, filed on Jan. 13, 2003, now Pat. No. 6,852,044, which

is a continuation-in-part of application No. 10/002,641, filed on Nov. 28, 2001, now Pat. No. 6,547,677.

(51) **Int. Cl.**
A63B 37/06 (2006.01)
(52) **U.S. Cl.**
USPC **473/376**
(58) **Field of Classification Search**
USPC **473/376**
See application file for complete search history.

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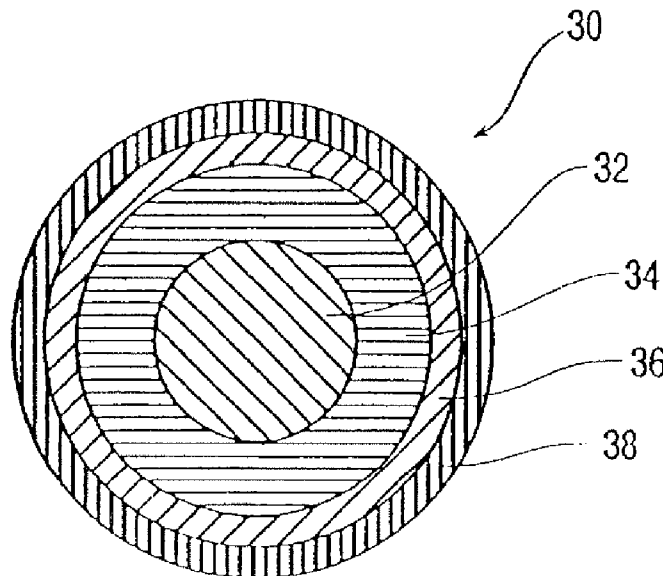
Primary Examiner — Raeann Gorden

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(57) **ABSTRACT**

Golf balls consisting of a dual core and a dual cover are disclosed. The dual core consists of an inner core layer formed from a rubber composition and an outer core layer formed from a highly neutralized polymer composition.

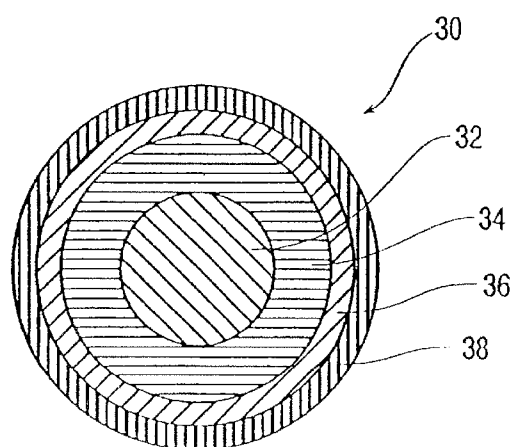
20 Claims, 1 Drawing Sheet



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MULTI-LAYER GOLF BALL

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 13/024,901, filed on Feb. 10, 2011, now U.S. Pat. No. 8,123,632 which is a continuation of U.S. patent application Ser. No. 12/233,776, filed Sep. 19, 2008, now U.S. Pat. No. 7,887,437, which is a continuation-in-part of U.S. patent application Ser. No. 12/048,003, filed Mar. 13, 2008, now abandoned which is a continuation-in-part of U.S. patent application Ser. No. 11/767,070, filed Jun. 22, 2007, now abandoned which is a continuation-in-part of U.S. patent application Ser. No. 10/773,906, filed Feb. 6, 2004, now U.S. Pat. No. 7,255,656, which is a continuation-in-part of U.S. patent application Ser. No. 10/341,574, filed Jan. 13, 2003, now U.S. Pat. No. 6,852,044, which is a continuation-in-part of U.S. patent application Ser. No. 10/002,641, filed Nov. 28, 2001, now U.S. Pat. No. 6,547,677. The entire disclosure of each of these references is hereby incorporated herein by reference.

FIELD OF THE INVENTION

The present invention generally relates to golf balls, and more particularly to golf balls having dual cores surrounded by dual covers, wherein the outer surface hardness of the outer core layer is greater than the material hardness of the inner cover layer.

BACKGROUND OF THE INVENTION

Numerous golf balls having a multilayer construction wherein the core hardness and cover hardness have been variously improved are disclosed in the prior art. For example, U.S. Pat. No. 6,987,159 to Iwami discloses a solid golf ball with a solid core and a polyurethane cover, wherein the difference in Shore D hardness between a center portion and a surface portion of the solid core is at least 15, the polyurethane cover has a thickness (t) of not more than 1.0 mm and is formed from a cured urethane composition having a Shore D hardness (D) of from 35 to 60, and a product of t and D ranges from 10 to 45.

U.S. Pat. No. 7,175,542 to Watanabe et al. discloses a multi-piece solid golf ball composed of a multilayer core having at least an inner core layer and an outer core layer, one or more cover layers which enclose the core, and numerous dimples formed on a surface of the cover layer. The golf ball is characterized in that the following hardness conditions are satisfied: (1) (JIS-C hardness of cover)–(JIS-C hardness at center of core) ≥ 27 , (2) $23 \leq$ (JIS-C hardness at surface of core)–(JIS-C hardness at center of core) ≤ 40 , and (3) $0.50 \leq$ [(deflection amount of entire core)/(deflection amount of inner core layer)] ≤ 0.75 .

U.S. Pat. No. 6,679,791 to Watanabe discloses a multi-piece golf ball which includes a rubbery elastic core, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer between the core and the cover. The intermediate layer is composed of a resin material which is harder than the cover. The elastic core has a hardness which gradually increases radially outward from the center to the surface thereof. The center and surface of the elastic core have a hardness difference of at least 18 JIS-C hardness units.

U.S. Pat. No. 5,782,707 to Yamagishi et al. discloses a three-piece solid golf ball consisting of a solid core, an intermediate layer, and a cover, wherein the hardness is measured

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by a JIS-C scale hardness meter, the core center hardness is up to 75 degrees, the core surface hardness is up to 85 degrees, the core surface hardness is higher than the core center hardness by 8 to 20 degrees, the intermediate layer hardness is higher than the core surface hardness by at least 5 degrees, and the cover hardness is lower than the intermediate layer hardness by at least 5 degrees.

Additional examples can be found, for example, in U.S. Pat. No. 6,686,436 to Iwami, U.S. Pat. No. 6,786,836 to Higuchi et al., U.S. Pat. No. 7,086,969 to Higuchi et al., U.S. Pat. No. 7,153,224 to Higuchi et al., and U.S. Pat. No. 7,226,367 to Higuchi et al.

The present invention provides a novel multilayer golf ball construction which provides desirable spin and distance properties.

SUMMARY OF THE INVENTION

In one embodiment, the present invention is directed to a golf ball consisting of an inner core layer, an outer core layer, an inner cover layer, and an outer cover layer. The inner core layer is formed from a rubber composition and has a diameter of from 1.200 inches to 1.300 inches, a center hardness (H_{center}) of 50 Shore C or greater, and an outer surface hardness of 65 Shore C or greater. The outer core layer is formed from a highly neutralized polymer composition and has an outer surface hardness ($H_{outer\ core}$) of 75 Shore C or greater. The inner cover layer is formed from a thermoplastic composition and has a material hardness ($H_{inner\ cover}$) less than the outer surface hardness of the outer core layer. The outer cover layer is formed from a composition selected from the group consisting of polyurethanes, polyureas, and copolymers and blends thereof.

In another embodiment, the present invention is directed to a golf ball comprising a core and a cover. The core consists of an inner core layer and an outer core layer. The inner core layer is formed from a rubber composition and has a diameter of from 1.200 inches to 1.300 inches, a center hardness (H_{center}) of from 50 Shore C to 70 Shore C, and an outer surface hardness of from 60 Shore C to 85 Shore C. The outer core layer is formed from a highly neutralized polymer composition and has an outer surface hardness ($H_{outer\ core}$) of from 80 Shore C to 95 Shore C. The cover consists of an inner cover layer and an outer cover layer. The inner cover layer is formed from a thermoplastic composition and has a material hardness ($H_{inner\ cover}$) less than the outer surface hardness of the outer core layer. The outer cover layer is formed from a composition selected from the group consisting of polyurethanes, polyureas, and copolymers and blends thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a golf ball according to an embodiment of the present invention.

DETAILED DESCRIPTION

FIG. 1 shows a golf ball 30 according to an embodiment of the present invention, including an inner core layer 32, an outer core layer 34, an inner cover layer 36, and an outer cover layer 38.

A golf ball having a dual core (i.e., two-layer core) and a dual cover (i.e., two-layer cover) enclosing the core is disclosed. The dual core consists of an inner core layer and an outer core layer. The inner core layer has a diameter within a range having a lower limit of 0.750 or 1.000 or 1.100 or 1.200 inches and an upper limit of 1.300 or 1.350 or 1.400 inches.

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The outer core layer encloses the inner core layer such that the two-layer core has an overall diameter within a range having a lower limit of 1.400 or 1.500 or 1.510 or 1.520 or 1.525 inches and an upper limit of 1.540 or 1.550 or 1.555 or 1.560 or 1.590 inches. In a particular embodiment, the inner core layer has a diameter of 1.250 inches and the outer core layer encloses the inner core layer such that the two-layer core has an overall diameter of 1.530 inches or 1.550 inches.

The inner core layer has a center hardness (H_{center}) of 45 Shore C or greater, or 50 Shore C or greater, or 55 Shore C or greater, or 60 Shore C or greater, or a center hardness within a range having a lower limit of 40 or 45 or 50 or 55 or 60 Shore C and an upper limit of 65 or 70 or 75 or 80 Shore C. The inner core layer has an outer surface hardness of 65 Shore C or greater, or 70 Shore C or greater, or 75 Shore C or greater, or 80 Shore C or greater, or an outer surface hardness within a range having a lower limit of 55 or 60 or 65 or 70 or 75 Shore C and an upper limit of 80 or 85 or 90 Shore C. In a particular embodiment, the Shore C hardness of the inner core layer's outer surface is greater than or equal to the center Shore C hardness. In another particular embodiment, the inner core layer has a positive hardness gradient wherein the Shore C hardness of the inner core layer's outer surface is at least 10 Shore C units greater, or at least 15 Shore C units greater, or 19 Shore C units greater than the center Shore C hardness.

The outer core layer has an outer surface hardness ($H_{outer\ core}$) of 75 Shore C or greater, or 80 Shore C or greater, or greater than 80 Shore C, or 85 Shore C or greater, or greater than 85 Shore C, or 87 Shore C or greater, or greater than 87 Shore C, or 89 Shore C or greater, or greater than 89 Shore C, or 90 Shore C or greater, or greater than 90 Shore C, or an outer surface hardness within a range having a lower limit of 75 or 80 or 85 or 90 Shore C and an upper limit of 95 Shore C. In a particular embodiment, the overall dual core has a positive hardness gradient wherein the Shore C hardness of the outer core layer's outer surface is at least 20 Shore C units greater, or at least 25 Shore C units greater, or at least 30 Shore C units greater, than the inner core layer's center Shore C hardness. In another particular embodiment, the Shore C hardness of the outer core layer's outer surface is greater than the material hardness of the inner cover layer.

For purposes of the present disclosure, the center hardness of the inner core layer is obtained according to the following procedure. The core is gently pressed into a hemispherical holder having an internal diameter approximately slightly smaller than the diameter of the core, such that the core is held in place in the hemispherical portion of the holder while concurrently leaving the geometric central plane of the core exposed. The core is secured in the holder by friction, such that it will not move during the cutting and grinding steps, but the friction is not so excessive that distortion of the natural shape of the core would result. The core is secured such that the parting line of the core is roughly parallel to the top of the holder. The diameter of the core is measured 90 degrees to this orientation prior to securing. A measurement is also made from the bottom of the holder to the top of the core to provide a reference point for future calculations. A rough cut is made slightly above the exposed geometric center of the core using a band saw or other appropriate cutting tool, making sure that the core does not move in the holder during this step. The remainder of the core, still in the holder, is secured to the base plate of a surface grinding machine. The exposed 'rough' surface is ground to a smooth, flat surface, revealing the geometric center of the core, which can be verified by measuring the height from the bottom of the holder to the exposed surface of the core, making sure that exactly half of the original height of the core, as measured above, has been

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removed to within ± 0.004 inches. Leaving the core in the holder, the center of the core is found with a center square and carefully marked and the hardness is measured at the center mark according to ASTM D-2240. Additional hardness measurements at any distance from the center of the core can then be made by drawing a line radially outward from the center mark, and measuring the hardness at any given distance along the line, typically in 2 mm increments from the center. The hardness at a particular distance from the center should be measured along at least two, preferably four, radial arms located 180° apart, or 90° apart, respectively, and then averaged. All hardness measurements performed on a plane passing through the geometric center are performed while the core is still in the holder and without having disturbed its orientation, such that the test surface is constantly parallel to the bottom of the holder, and thus also parallel to the properly aligned foot of the durometer.

For purposes of the present disclosure, the outer surface hardness of a golf ball layer is measured on the actual outer surface of the layer and is obtained from the average of a number of measurements taken from opposing hemispheres, taking care to avoid making measurements on the parting line of the core or on surface defects, such as holes or protrusions. Hardness measurements are made pursuant to ASTM D-2240 "Indentation Hardness of Rubber and Plastic by Means of a Durometer." Because of the curved surface, care must be taken to insure that the golf ball or golf ball subassembly is centered under the durometer indenter before a surface hardness reading is obtained. A calibrated, digital durometer, capable of reading to 0.1 hardness units is used for all hardness measurements and is set to take hardness readings at 1 second after the maximum reading is obtained. The digital durometer must be attached to, and its foot made parallel to, the base of an automatic stand. The weight on the durometer and attack rate conform to ASTM D-2240.

For purposes of the present disclosure, a hardness gradient of a golf ball layer is defined by hardness measurements made at the outer surface of the layer and the inner surface of the layer. "Negative" and "positive" refer to the result of subtracting the hardness value at the innermost surface of the golf ball component from the hardness value at the outermost surface of the component. For example, if the outer surface of a solid core has a lower hardness value than the center (i.e., the surface is softer than the center), the hardness gradient will be deemed a "negative" gradient.

Thermoplastic layers of golf balls disclosed herein may be treated in such a manner as to create a positive or negative hardness gradient, as disclosed, for example, in U.S. patent application Ser. No. 11/939,632, filed Nov. 14, 2007; Ser. No. 11/939,634, filed Nov. 14, 2007; Ser. No. 11/939,635, filed Nov. 14, 2007; and Ser. No. 11/939,637 filed Nov. 14, 2007. The entire disclosure of each of these references is hereby incorporated herein by reference. In golf ball layers of the present invention wherein a thermosetting rubber is used, gradient-producing processes and/or gradient-producing rubber formulations may be employed, as disclosed, for example, in U.S. patent application Ser. No. 12/048,665, filed Mar. 14, 2008; Ser. No. 11/829,461, filed Jul. 27, 2007; Ser. No. 11/772,903, filed Jul. 3, 2007; Ser. No. 11/832,163, filed Aug. 1, 2007; and U.S. Pat. No. 7,410,429. The entire disclosure of each of these references is hereby incorporated herein by reference.

The inner core layer is preferably formed from a rubber composition. Suitable rubber compositions include natural and synthetic rubbers including, but not limited to, polybutadiene, polyisoprene, ethylene propylene rubber ("EPR"), styrene-butadiene rubber, styrenic block copolymer rubbers

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(such as SI, SIS, SB, SBS, SIBS, and the like, where "S" is styrene, "I" is isobutylene, and "B" is butadiene), butyl rubber, halobutyl rubber, polystyrene elastomers, polyethylene elastomers, polyurethane elastomers, polyurea elastomers, metallocene-catalyzed elastomers and plastomers, copolymers of isobutylene and para-alkylstyrene, halogenated copolymers of isobutylene and para-alkylstyrene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and combinations of two or more thereof. Diene rubbers are preferred, particularly polybutadiene, styrene-butadiene, and mixtures of polybutadiene with other elastomers wherein the amount of polybutadiene present is at least 40 wt % based on the total polymeric weight of the mixture. Suitable polybutadiene-based and styrene-butadiene-based rubber core compositions preferably comprise the base rubber, an initiator agent, and a coagent. Suitable examples of commercially available polybutadienes include, but are not limited to, Buna CB neodymium catalyzed polybutadiene rubbers, such as Buna CB 23, and Tak-
tene® cobalt catalyzed polybutadiene rubbers, such as Tak-
tene® 220 and 221, commercially available from LANXESS® Corporation; SE BR-1220, commercially avail-
able from The Dow Chemical Company; Europrene® NEO-
CIS® BR 40 and BR 60, commercially available from Polimeri Europa®; UBEPOL-BR® rubbers, commercially
available from UBE Industries, Inc.; BR 01, commercially
available from Japan Synthetic Rubber Co., Ltd.; and
Neodene neodymium catalyzed high cis polybutadiene rub-
bers, such as Neodene BR 40, commercially available from
Karbochem.

Suitable initiator agents include organic peroxides, high energy radiation sources capable of generating free radicals, and combinations thereof. High energy radiation sources capable of generating free radicals include, but are not limited to, electron beams, ultra-violet radiation, gamma radiation, X-ray radiation, infrared radiation, heat, and combinations thereof. Suitable organic peroxides include, but are not limited to, dicumyl peroxide; n-butyl-4,4-di(t-butylperoxy)val-
erate; 1,1-di(t-butylperoxy)3,3,5-trimethylcyclohexane; 2,5-
dimethyl-2,5-di(t-butylperoxy)hexane; di-t-butyl peroxide;
di-t-amyl peroxide; t-butyl peroxide; t-butyl cumyl peroxide;
2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3; di(2-t-butyl-
peroxyisopropyl)benzene; dilauroyl peroxide; dibenzoyl per-
oxide; t-butyl hydroperoxide; lauryl peroxide; benzoyl per-
oxide; and combinations thereof. In a particular embodiment,
the initiator agent is dicumyl peroxide, including, but not
limited to Perkadox® BC, commercially available from Akzo
Nobel. Peroxide initiator agents are generally present in the
rubber composition in an amount of at least 0.05 parts by
weight per 100 parts of the base rubber, or an amount within
the range having a lower limit of 0.05 parts or 0.1 parts or 1
part or 1.25 parts or 1.5 parts by weight per 100 parts of the
base rubber, and an upper limit of 2.5 parts or 3 parts or 5 parts
or 6 parts or 10 parts or 15 parts by weight per 100 parts of the
base rubber.

Coagents are commonly used with peroxides to increase the state of cure. Suitable coagents include, but are not limited to, metal salts of unsaturated carboxylic acids; unsaturated vinyl compounds and polyfunctional monomers (e.g., trimethylolpropane trimethacrylate); phenylene bismaleimide; and combinations thereof. Particular examples of suitable metal salts include, but are not limited to, one or more metal salts of acrylates, diacrylates, methacrylates, and dimethacrylates, wherein the metal is selected from magnesium, calcium, zinc, aluminum, lithium, nickel, and sodium. In a particular embodiment, the coagent is selected from zinc salts of

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acrylates, diacrylates, methacrylates, dimethacrylates, and mixtures thereof. In another particular embodiment, the coagent is zinc diacrylate. When the coagent is zinc diacrylate and/or zinc dimethacrylate, the coagent is typically included in the rubber composition in an amount within the range having a lower limit of 1 or 5 or 10 or 15 or 19 or 20 parts by weight per 100 parts of the base rubber, and an upper limit of 24 or 25 or 30 or 35 or 40 or 45 or 50 or 60 parts by weight per 100 parts of the base rubber. When one or more less active coagents are used, such as zinc monomethacrylate and various liquid acrylates and methacrylates, the amount of less active coagent used may be the same as or higher than for zinc diacrylate and zinc dimethacrylate coagents. The desired compression may be obtained by adjusting the amount of crosslinking, which can be achieved, for example, by altering the type and amount of coagent. The rubber composition optionally includes a curing agent. Suitable curing agents include, but are not limited to, sulfur; N-oxydiethylene 2-benzothiazole sulfenamide; N,N-di-ortho-tolylguanidine; bismuth dimethyldithiocarbamate; N-cyclohexyl 2-benzothiazole sulfenamide; N,N-diphenylguanidine; 4-morpholinyl-2-benzothiazole disulfide; dipentamethylenethiuram hexasulfide; thiuram disulfides; mercaptobenzothiazoles; sulfenamides; dithiocarbamates; thiuram sulfides; guanidines; thioureas; xanthates; dithiophosphates; aldehyde-amines; dibenzothiazyl disulfide; tetraethylthiuram disulfide; tetrabutylthiuram disulfide; and combinations thereof.

The rubber composition optionally contains one or more antioxidants. Antioxidants are compounds that can inhibit or prevent the oxidative degradation of the rubber. Some antioxidants also act as free radical scavengers; thus, when antioxidants are included in the rubber composition, the amount of initiator agent used may be as high or higher than the amounts disclosed herein. Suitable antioxidants include, for example, dihydroquinoline antioxidants, amine type antioxidants, and phenolic type antioxidants.

The rubber composition may contain one or more fillers to adjust the density and/or specific gravity of the core. Exemplary fillers include precipitated hydrated silica, clay, talc, asbestos, glass fibers, aramid fibers, mica, calcium metasilicate, zinc sulfate, barium sulfate, zinc sulfide, lithopone, silicates, silicon carbide, diatomaceous earth, polyvinyl chloride, carbonates (e.g., calcium carbonate, zinc carbonate, barium carbonate, and magnesium carbonate), metals (e.g., titanium, tungsten, aluminum, bismuth, nickel, molybdenum, iron, lead, copper, boron, cobalt, beryllium, zinc, and tin), metal alloys (e.g., steel, brass, bronze, boron carbide whiskers, and tungsten carbide whiskers), oxides (e.g., zinc oxide, tin oxide, iron oxide, calcium oxide, aluminum oxide, titanium dioxide, magnesium oxide, and zirconium oxide), particulate carbonaceous materials (e.g., graphite, carbon black, cotton flock, natural bitumen, cellulose flock, and leather fiber), microballoons (e.g., glass and ceramic), fly ash, regrind (i.e., core material that is ground and recycled), nanofillers and combinations thereof. The amount of particulate material(s) present in the rubber composition is typically within a range having a lower limit of 5 parts or 10 parts by weight per 100 parts of the base rubber, and an upper limit of 30 parts or 50 parts or 100 parts by weight per 100 parts of the base rubber. Filler materials may be dual-functional fillers, such as zinc oxide (which may be used as a filler/acid scavenger) and titanium dioxide (which may be used as a filler/brightener material).

The rubber composition may also contain one or more additives selected from processing aids, processing oils, plasticizers, coloring agents, fluorescent agents, chemical blowing and foaming agents, defoaming agents, stabilizers, soft-

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ening agents, impact modifiers, free radical scavengers, accelerators, scorch retarders, and the like. The amount of additive(s) typically present in the rubber composition is typically within a range having a lower limit of 0 parts by weight per 100 parts of the base rubber, and an upper limit of 20 parts or 50 parts or 100 parts or 150 parts by weight per 100 parts of the base rubber.

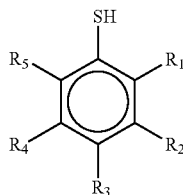
The rubber composition optionally includes a soft and fast agent. As used herein, "soft and fast agent" means any compound or a blend thereof that is capable of making a core 1) softer (have a lower compression) at a constant COR and/or 2) faster (have a higher COR) at equal compression, when compared to a core equivalently prepared without a soft and fast agent.

Preferably, the rubber composition contains from 0.05 phr to 10.0 phr of a soft and fast agent. In one embodiment, the soft and fast agent is present in an amount within a range having a lower limit of 0.05 or 0.1 or 0.2 or 0.5 phr and an upper limit of 1.0 or 2.0 or 3.0 or 5.0 phr. In another embodiment, the soft and fast agent is present in an amount of from 2.0 phr to 5.0 phr, or from 2.35 phr to 4.0 phr, or from 2.35 phr to 3.0 phr. In an alternative high concentration embodiment, the soft and fast agent is present in an amount of from 5.0 phr to 10.0 phr, or from 6.0 phr to 9.0 phr, or from 7.0 phr to 8.0 phr. In another embodiment, the soft and fast agent is present in an amount of 2.6 phr.

Suitable soft and fast agents include, but are not limited to, organosulfur and metal-containing organosulfur compounds; organic sulfur compounds, including mono, di, and polysulfides, thiol, and mercapto compounds; inorganic sulfide compounds; blends of an organosulfur compound and an inorganic sulfide compound; Group VIA compounds; substituted and unsubstituted aromatic organic compounds that do not contain sulfur or metal; aromatic organometallic compounds; hydroquinones; benzoquinones; quinhydrones; catechols; resorcinols; and combinations thereof.

As used herein, "organosulfur compound" refers to any compound containing carbon, hydrogen, and sulfur, where the sulfur is directly bonded to at least 1 carbon. As used herein, the term "sulfur compound" means a compound that is elemental sulfur, polymeric sulfur, or a combination thereof. It should be further understood that the term "elemental sulfur" refers to the ring structure of S₈ and that "polymeric sulfur" is a structure including at least one additional sulfur relative to elemental sulfur.

Particularly suitable as soft and fast agents are organosulfur compounds having the following general formula:



where R₁-R₅ can be C₁-C₈ alkyl groups; halogen groups; thiol groups (-SH), carboxylated groups; sulfonated groups; and hydrogen; in any order; and also pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-

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chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; zinc salts thereof; non-metal salts thereof, for example, ammonium salt of pentachlorothiophenol; magnesium pentachlorothiophenol; cobalt pentachlorothiophenol; and combinations thereof. Preferably, the halogenated thiophenol compound is pentachlorothiophenol, which is commercially available in neat form or under the tradename STRUKTOL®, a clay-based carrier containing the sulfur compound pentachlorothiophenol loaded at 45 percent (correlating to 2.4 parts PCTP). STRUKTOL® is commercially available from Struktol Company of America of Stow, Ohio. PCTP is commercially available in neat form from eChinacem of San Francisco, Calif. and in the salt form from eChinacem of San Francisco, Calif. Most preferably, the halogenated thiophenol compound is the zinc salt of pentachlorothiophenol, which is commercially available from eChinacem of San Francisco, Calif. Suitable organosulfur compounds are further disclosed, for example, in U.S. Pat. Nos. 6,635,716, 6,919,393, 7,005,479 and 7,148,279, the entire disclosures of which are hereby incorporated herein by reference.

Suitable metal-containing organosulfur compounds include, but are not limited to, cadmium, copper, lead, and tellurium analogs of diethyldithiocarbamate, diamyldithiocarbamate, and dimethyldithiocarbamate, and combinations thereof. Additional examples are disclosed in U.S. Pat. No. 7,005,479, the entire disclosure of which is hereby incorporated herein by reference.

Suitable disulfides include, but are not limited to, 4,4'-diphenyl disulfide; 4,4'-ditolyl disulfide; 2,2'-benzamido diphenyl disulfide; bis(2-aminophenyl)disulfide; bis(4-aminophenyl)disulfide; bis(3-aminophenyl) disulfide; 2,2'-bis(4-aminonaphthyl)disulfide; 2,2'-bis(3-aminonaphthyl)disulfide; 2,2'-bis(4-aminonaphthyl)disulfide; 2,2'-bis(5-aminonaphthyl)disulfide; 2,2'-bis(6-aminonaphthyl)disulfide; 2,2'-bis(7-aminonaphthyl)disulfide; 2,2'-bis(8-aminonaphthyl)disulfide; 1,1'-bis(2-aminonaphthyl)disulfide; 1,1'-bis(3-aminonaphthyl) disulfide; 1,1'-bis(3-aminonaphthyl)disulfide; 1,1'-bis(4-aminonaphthyl)disulfide; 1,1'-bis(5-aminonaphthyl)disulfide; 1,1'-bis(6-aminonaphthyl)disulfide; 1,1'-bis(7-aminonaphthyl)disulfide; 1,1'-bis(8-aminonaphthyl)disulfide; 1,2'-diamino-1,2'-dithiodinaphthalene; 2,3'-diamino-1,2'-dithiodinaphthalene; bis(4-chlorophenyl)disulfide; bis(2-chlorophenyl)disulfide; bis(3-chlorophenyl)disulfide; bis(4-bromophenyl)disulfide; bis(2-bromophenyl)disulfide; bis(3-bromophenyl)disulfide; bis(4-fluorophenyl)disulfide; bis(4-iodophenyl)disulfide; bis(2,5-dichlorophenyl)disulfide; bis(3,5-dichlorophenyl)disulfide; bis(2,4-dichlorophenyl)disulfide; bis(2,6-dichlorophenyl)disulfide; bis(2,5-dibromophenyl)disulfide; bis(3,5-dibromophenyl)disulfide; bis(2-chloro-5-bromophenyl)disulfide; bis(2,4,6-trichlorophenyl)disulfide; bis(2,3,4,5,6-pentachlorophenyl)disulfide; bis(4-cyanophenyl)disulfide; bis(2-cyanophenyl)disulfide; bis(4-nitrophenyl)disulfide; bis(2-nitrophenyl)disulfide; 2,2'-dithiobenzoic acid ethylester; 2,2'-dithiobenzoic acid methylester; 2,2'-dithiobenzoic acid; 4,4'-dithiobenzoic acid ethylester; bis(4-acetylphenyl)disulfide; bis(2-acetylphenyl)disulfide; bis(4-formylphenyl)disulfide; bis(4-carbamoylphenyl)disulfide; 1,1'-dinaphthyl disulfide;

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2,2'-dinaphthyl disulfide; 1,2'-dinaphthyl disulfide; 2,2'-bis(1-chlorodinaphthyl)disulfide; 2,2'-bis(1-bromonaphthyl)disulfide; 1,1'-bis(2-chloronaphthyl)disulfide; 2,2'-bis(1-cyanonaphthyl)disulfide; 2,2'-bis(1-acetylnaphthyl)disulfide; and the like; and combinations thereof.

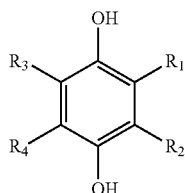
Suitable inorganic sulfide compounds include, but are not limited to, titanium sulfide, manganese sulfide, and sulfide analogs of iron, calcium, cobalt, molybdenum, tungsten, copper, selenium, yttrium, zinc, tin, and bismuth.

Suitable Group VIA compounds include, but are not limited to, elemental sulfur and polymeric sulfur, such as those which are commercially available from Elastochem, Inc. of Chardon, Ohio; sulfur catalyst compounds which include PB(RM-S)-80 elemental sulfur and PB(CRST)-65 polymeric sulfur, each of which is available from Elastochem, Inc; tellurium catalysts, such as TELLOY®, and selenium catalysts, such as VANDEX®, each of which is commercially available from RT Vanderbilt.

Suitable substituted and unsubstituted aromatic organic components that do not include sulfur or a metal include, but are not limited to, 4,4'-diphenyl acetylene, azobenzene, and combinations thereof. The aromatic organic group preferably ranges in size from C₆ to C₂₀, and more preferably from C₆ to C₁₀.

Suitable substituted and unsubstituted aromatic organometallic compounds include, but are not limited to, those having the formula (R₁)_x—R₃—M—R₄—(R₂)_y, wherein R₁ and R₂ are each hydrogen or a substituted or unsubstituted C₁₋₂₀ linear, branched, or cyclic alkyl, alkoxy, or alkylthio group, or a single, multiple, or fused ring C₆ to C₂₄ aromatic group; x and y are each an integer from 0 to 5; R₃ and R₄ are each selected from a single, multiple, or fused ring C₆ to C₂₄ aromatic group; and M includes an azo group or a metal component. Preferably, R₃ and R₄ are each selected from a C₆ to C₁₀ aromatic group, more preferably selected from phenyl, benzyl, naphthyl, benzamido, and benzothiazyl. Preferably R₁ and R₂ are each selected from substituted and unsubstituted C₁₋₁₀ linear, branched, and cyclic alkyl, alkoxy, and alkylthio groups, and C₆ to C₁₀ aromatic groups. When R₁, R₂, R₃, and R₄ are substituted, the substitution may include one or more of the following substituent groups: hydroxy and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carboxyl including esters, acids, and metal salts thereof; silyl; acrylates and metal salts thereof; sulfonyl and sulfonamide; and phosphates and phosphites. When M is a metal component, it may be any suitable elemental metal. The metal is generally a transition metal, and is preferably tellurium or selenium.

Suitable hydroquinones include, but are not limited to, compounds represented by the following formula, and hydrates thereof:

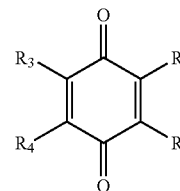


wherein each R₁, R₂, R₃, and R₄ is independently selected from the group consisting of hydrogen, a halogen group (F, Cl, Br, I), an alkyl group, a carboxyl group (—COOH) and metal salts thereof (e.g., —COO[−]M⁺) and esters thereof (—COOR), an acetate group

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(—CH₂COOH) and esters thereof (—CH₂COOR), a formyl group (—CHO), an acyl group (—COR), an acetyl group (—COCH₃), a halogenated carbonyl group (—COX), a sulfo group (—SO₃H) and esters thereof (—SO₃R), a halogenated sulfonyl group (—SO₂X), a sulfino group (—SO₂H), an alkylsulfinyl group (—SOR), a carbamoyl group (—CONH₂), a halogenated alkyl group, a cyano group (—CN), an alkoxy group (—OR), a hydroxy group (—OH) and metal salts thereof (e.g., —O[−]M⁺), an amino group (—NH₂), a nitro group (—NO₂), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl (—C(CH₃)₂-phenyl); benzyl (—CH₂-phenyl)], a nitroso group (—NO), an acetamido group (—NHCOCH₃), and a vinyl group (—CH=CH₂). Particularly preferred hydroquinones include compounds represented by the above formula, and hydrates thereof, wherein each R₁, R₂, R₃, and R₄ is independently selected from the group consisting of: a metal salt of a carboxyl group (e.g., —COO[−]M⁺), an acetate group (—CH₂COOH) and esters thereof (—CH₂COOR), a hydroxy group (—OH), a metal salt of a hydroxy group (e.g., —O[−]M⁺), an amino group (—NH₂), a nitro group (—NO₂), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl (—C(CH₃)₂-phenyl); benzyl (—CH₂-phenyl)], a nitroso group (—NO), an acetamido group (—NHCOCH₃), and a vinyl group (—CH=CH₂). Examples of particularly suitable hydroquinones include, but are not limited to, hydroquinone; tetrachlorohydroquinone; 2-chlorohydroquinone; 2-bromohydroquinone; 2,5-dichlorohydroquinone; 2,5-dibromohydroquinone; tetrabromohydroquinone; 2-methylhydroquinone; 2-t-butylhydroquinone; 2,5-di-t-amylhydroquinone; and 2-(2-chlorophenyl)hydroquinone hydrate. Hydroquinone and tetrachlorohydroquinone are particularly preferred, and even more particularly preferred is 2-(2-chlorophenyl)hydroquinone hydrate. Suitable hydroquinones are further disclosed, for example, in U.S. Patent Application Publication No. 2007/0213440, the entire disclosure of which is hereby incorporated herein by reference.

Suitable benzoquinones include compounds represented by the following formula, and hydrates thereof:



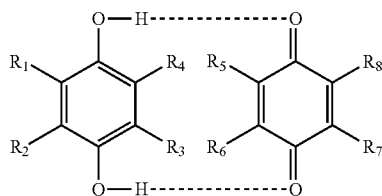
wherein each R₁, R₂, R₃, and R₄ is independently selected from the group consisting of hydrogen, a halogen group (F, Cl, Br, I), an alkyl group, a carboxyl group (—COOH) and metal salts thereof (e.g., —COO[−]M⁺) and esters thereof (—COOR), an acetate group (—CH₂COOH) and esters thereof (—CH₂COOR), a formyl group (—CHO), an acyl group (—COR), an acetyl group (—COCH₃), a halogenated carbonyl group (—COX), a sulfo group (—SO₃H) and esters thereof (—SO₃R), a halogenated sulfonyl group (—SO₂X), a sulfino group (—SO₂H), an alkylsulfinyl group (—SOR), a carbamoyl group (—CONH₂), a haloge-

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nated alkyl group, a cyano group ($-\text{CN}$), an alkoxy group ($-\text{OR}$), a hydroxy group ($-\text{OH}$) and metal salts thereof (e.g., $-\text{O}^-\text{M}^+$), an amino group ($-\text{NH}_2$), a nitro group ($-\text{NO}_2$), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl ($-\text{C}(\text{CH}_3)_2\text{phenyl}$); benzyl ($-\text{CH}_2\text{phenyl}$)], a nitroso group ($-\text{NO}$), an acetamido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). Particularly preferred benzoquinones include compounds represented by the above formula, and hydrates thereof, wherein each R_1 , R_2 , R_3 , and R_4 is independently selected from the group consisting of: a metal salt of a carboxyl group (e.g., $-\text{COO}^-\text{M}^+$), an acetate group ($-\text{CH}_2\text{COOH}$) and esters thereof ($-\text{CH}_2\text{COOR}$), a hydroxy group ($-\text{OH}$), a metal salt of a hydroxy group (e.g., $-\text{O}^-\text{M}^+$), an amino group ($-\text{NH}_2$), a nitro group ($-\text{NO}_2$), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl ($-\text{C}(\text{CH}_3)_2\text{phenyl}$); benzyl ($-\text{CH}_2\text{phenyl}$)], a nitroso group ($-\text{NO}$), an acetamido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). Methyl p-benzoquinone and tetrachloro p-benzoquinone are more particularly preferred. Suitable benzoquinones are further disclosed, for example, in U.S. Patent Application Publication No. 2007/0213442, the entire disclosure of which is hereby incorporated herein by reference.

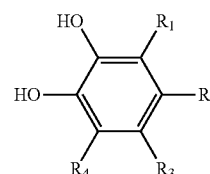
Suitable quinhydrones include, but are not limited to, compounds represented by the following formula, and hydrates thereof:



wherein each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 is independently selected from the group consisting of hydrogen, a halogen group (F, Cl, Br, I), an alkyl group, a carboxyl group ($-\text{COOH}$) and metal salts thereof (e.g., $-\text{COO}^-\text{M}^+$) and esters thereof ($-\text{COOR}$), an acetate group ($-\text{CH}_2\text{COOH}$) and esters thereof ($-\text{CH}_2\text{COOR}$), a formyl group ($-\text{CHO}$), an acyl group ($-\text{COR}$), an acetyl group ($-\text{COCH}_3$), a halogenated carbonyl group ($-\text{COX}$), a sulfo group ($-\text{SO}_3\text{H}$) and esters thereof ($-\text{SO}_3\text{R}$), a halogenated sulfonyl group ($-\text{SO}_2\text{X}$), a sulfino group ($-\text{SO}_2\text{H}$), an alkylsulfanyl group ($-\text{SOR}$), a carbamoyl group ($-\text{CONH}_2$), a halogenated alkyl group, a cyano group ($-\text{CN}$), an alkoxy group ($-\text{OR}$), a hydroxy group ($-\text{OH}$) and metal salts thereof (e.g., $-\text{O}^-\text{M}^+$), an amino group ($-\text{NH}_2$), a nitro group ($-\text{NO}_2$), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl ($-\text{C}(\text{CH}_3)_2\text{phenyl}$); benzyl ($-\text{CH}_2\text{phenyl}$)], a nitroso group ($-\text{NO}$), an acetamido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). Particularly preferred quinhydrones include compounds represented by the above formula, and hydrates thereof, wherein each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 is independently selected from the group consisting of: a metal salt of a carboxyl group (e.g., $-\text{COO}^-\text{M}^+$), an acetate group ($-\text{CH}_2\text{COOH}$) and

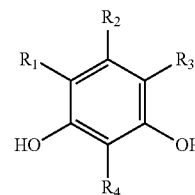
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esters thereof ($-\text{CH}_2\text{COOR}$), a hydroxy group ($-\text{OH}$), a metal salt of a hydroxy group (e.g., $-\text{O}^-\text{M}^+$), an amino group ($-\text{NH}_2$), a nitro group ($-\text{NO}_2$), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl ($-\text{C}(\text{CH}_3)_2\text{phenyl}$); benzyl ($-\text{CH}_2\text{phenyl}$)], a nitroso group ($-\text{NO}$), an acetamido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). Particularly preferred quinhydrones also include compounds represented by the above formula wherein each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 is hydrogen. Suitable quinhydrones are further disclosed, for example, in U.S. Patent Application Publication No. 2007/0213441, the entire disclosure of which is hereby incorporated herein by reference. Suitable catechols include compounds represented by the following formula, and hydrates thereof:



wherein each R_1 , R_2 , R_3 , and R_4 , is independently selected from the group consisting of hydrogen, a halogen group (F, Cl, Br, I), an alkyl group, a carboxyl group ($-\text{COOH}$) and metal salts thereof (e.g., $-\text{COO}^-\text{M}^+$) and esters thereof ($-\text{COOR}$), an acetate group ($-\text{CH}_2\text{COOH}$) and esters thereof ($-\text{CH}_2\text{COOR}$), a formyl group ($-\text{CHO}$), an acyl group ($-\text{COR}$), an acetyl group ($-\text{COCH}_3$), a halogenated carbonyl group ($-\text{COX}$), a sulfo group ($-\text{SO}_3\text{H}$) and esters thereof ($-\text{SO}_3\text{R}$), a halogenated sulfonyl group ($-\text{SO}_2\text{X}$), a sulfino group ($-\text{SO}_2\text{H}$), an alkylsulfanyl group ($-\text{SOR}$), a carbamoyl group ($-\text{CONH}_2$), a halogenated alkyl group, a cyano group ($-\text{CN}$), an alkoxy group ($-\text{OR}$), a hydroxy group ($-\text{OH}$) and metal salts thereof (e.g., $-\text{O}^-\text{M}^+$), an amino group ($-\text{NH}_2$), a nitro group ($-\text{NO}_2$), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl ($-\text{C}(\text{CH}_3)_2\text{phenyl}$); benzyl ($-\text{CH}_2\text{phenyl}$)], a nitroso group ($-\text{NO}$), an acetamido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). Suitable catechols are further disclosed, for example, in U.S. Patent Application Publication No. 2007/0213144, the entire disclosure of which is hereby incorporated herein by reference.

Suitable resorcinols include compounds represented by the following formula, and hydrates thereof:



wherein each R_1 , R_2 , R_3 , and R_4 , is independently selected from the group consisting of hydrogen, a halogen group (F, Cl, Br, I), an alkyl group, a carboxyl group ($-\text{COOH}$) and metal salts thereof (e.g., $-\text{COO}^-\text{M}^+$)

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and esters thereof ($-\text{COOR}$), an acetate group ($-\text{CH}_2\text{COOH}$) and esters thereof ($-\text{CH}_2\text{COOR}$), a formyl group ($-\text{CHO}$), an acyl group ($-\text{COR}$), an acetyl group ($-\text{COCH}_3$), a halogenated carbonyl group ($-\text{COX}$), a sulfo group ($-\text{SO}_3\text{H}$) and esters thereof ($-\text{SO}_3\text{R}$), a halogenated sulfonyl group ($-\text{SO}_2\text{X}$), a sulfino group ($-\text{SO}_2\text{H}$), an alkylsulfinyl group ($-\text{SOR}$), a carbamoyl group ($-\text{CONH}_2$), a halogenated alkyl group, a cyano group ($-\text{CN}$), an alkoxy group ($-\text{OR}$), a hydroxy group ($-\text{OH}$) and metal salts thereof (e.g., $-\text{O}^-\text{M}^+$), an amino group ($-\text{NH}_2$), a nitro group ($-\text{NO}_2$), an aryl group (e.g., phenyl, tolyl, etc.), an aryloxy group (e.g., phenoxy, etc.), an arylalkyl group [e.g., cumyl ($-\text{C}(\text{CH}_3)_2\text{phenyl}$); benzyl ($-\text{CH}_2\text{phenyl}$)], a nitroso group ($-\text{NO}$), an acetamido group ($-\text{NHCOCH}_3$), and a vinyl group ($-\text{CH}=\text{CH}_2$). 2-Nitroresorcinol is particularly preferred. Suitable resorcinols are further disclosed, for example, in U.S. Patent Application Publication No. 2007/0213144, the entire disclosure of which is hereby incorporated herein by reference.

When the rubber composition includes one or more hydroquinones, benzoquinones, quinhydrones, catechols, resorcinols, or a combination thereof, the total amount of hydroquinone(s), benzoquinone(s), quinhydrone(s), catechol(s), and/or resorcinol(s) present in the composition is typically at least 0.1 parts by weight or at least 0.15 parts by weight or at least 0.2 parts by weight per 100 parts of the base rubber, or an amount within the range having a lower limit of 0.1 parts or 0.15 parts or 0.25 parts or 0.3 parts or 0.375 parts by weight per 100 parts of the base rubber, and an upper limit of 0.5 parts or 1 part or 1.5 parts or 2 parts or 3 parts by weight per 100 parts of the base rubber.

In a particular embodiment, the soft and fast agent is selected from zinc pentachlorothiophenol, pentachlorothiophenol, ditolyl disulfide, diphenyl disulfide, dixylyl disulfide, 2-nitroresorcinol, and combinations thereof.

Suitable types and amounts of base rubber, initiator agent, coagent, filler, and additives are more fully described in, for example, U.S. Pat. Nos. 6,566,483, 6,695,718, and 6,939,907, 7,041,721 and 7,138,460, the entire disclosures of which are hereby incorporated herein by reference.

The outer core layer is preferably formed from a highly resilient thermoplastic polymer such as a highly neutralized polymer ("HNP") composition. HNP compositions suitable for use in forming the outer core layer of golf balls of the present invention preferably have a material hardness of 35 Shore D or greater, and more preferably have a hardness of 45 Shore D or greater or a hardness within a range having a lower limit of 45 or 50 or 55 or 57 or 58 or 60 or 65 or 70 or 75 Shore D and an upper limit of 80 or 85 or 90 or 95 Shore D.

Suitable HNP compositions for use in forming the outer core layer comprise an HNP and optionally melt flow modifier(s), additive(s), and/or filler(s). Suitable HNPs are salts of acid copolymers. It is understood that the HNP may be a blend of two or more HNPs. Preferred acid copolymers are copolymers of an α -olefin and a C_3 - C_8 α,β -ethylenically unsaturated carboxylic acid. The acid is typically present in the acid copolymer in an amount within a range having a lower limit of 1 or 10 or 12 or 15 or 20 wt % and an upper limit of 25 or 30 or 35 or 40 wt %, based on the total weight of the acid copolymer. The α -olefin is preferably selected from ethylene and propylene. The acid is preferably selected from (meth)acrylic acid, ethacrylic acid, maleic acid, crotonic acid, fumaric acid, and itaconic acid. (Meth)acrylic acid is particularly preferred. Suitable acid copolymers include partially neutralized acid polymers. Examples of suitable partially

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neutralized acid polymers include, but are not limited to, Surlyn® ionomers, commercially available from E. I. du Pont de Nemours and Company; AClyn® ionomers, commercially available from Honeywell International Inc.; and Iotek® ionomers, commercially available from ExxonMobil Chemical Company. Also suitable are DuPont® HPF 1000 and DuPont® HPF 2000, ionomeric materials commercially available from E. I. du Pont de Nemours and Company. In a preferred embodiment, the acid polymer of the HNP outer core layer composition has a modulus within a range having a lower limit of 25,000 or 27,000 or 30,000 or 40,000 or 45,000 or 50,000 or 55,000 or 60,000 psi and an upper limit of 72,000 or 75,000 or 100,000 or 150,000 psi. As used herein, "modulus" refers to flexural modulus as measured using a standard flex bar according to ASTM D790-B. Additional suitable acid polymers are more fully described, for example, in U.S. Pat. Nos. 6,562,906, 6,762,246, and 6,953,820 and U.S. Patent Application Publication Nos. 2005/0049367, 2005/0020741, and 2004/0220343, the entire disclosures of which are hereby incorporated herein by reference.

The HNP is formed by reacting the acid copolymer with a sufficient amount of cation source such that at least 80%, preferably at least 90%, more preferably at least 95%, and even more preferably 100%, of all acid groups present are neutralized. Suitable cation sources include metal ions and compounds of alkali metals, alkaline earth metals, and transition metals; metal ions and compounds of rare earth elements; silicone, silane, and silicate derivatives and complex ligands; and combinations thereof. Preferred cation sources are metal ions and compounds of magnesium, sodium, potassium, cesium, calcium, barium, manganese, copper, zinc, tin, lithium, and rare earth metals. Metal ions and compounds of calcium and magnesium are particularly preferred. The acid copolymer may be at least partially neutralized prior to contacting the acid copolymer with the cation source to form the HNP. Methods of preparing ionomers, and the acid copolymers on which ionomers are based, are disclosed, for example, in U.S. Pat. Nos. 3,264,272, and 4,351,931, and U.S. Patent Application Publication No. 2002/0013413.

HNP outer core layer compositions of the present invention optionally contain one or more melt flow modifiers. The amount of melt flow modifier in the composition is readily determined such that the melt flow index of the composition is at least 0.1 g/10 min, preferably from 0.5 g/10 min to 10.0 g/10 min, and more preferably from 1.0 g/10 min to 6.0 g/10 min, as measured using ASTM D-1238, condition E, at 190° C., using a 2160 gram weight.

Suitable melt flow modifiers include, but are not limited to, high molecular weight organic acids and salts thereof, polyamides, polyesters, polyacrylates, polyurethanes, polyethers, polyureas, polyhydric alcohols, and combinations thereof. Suitable organic acids are aliphatic organic acids, aromatic organic acids, saturated mono-functional organic acids, unsaturated monofunctional organic acids, multi-unsaturated mono-functional organic acids, and dimerized derivatives thereof. Particular examples of suitable organic acids include, but are not limited to, caproic acid, caprylic acid, capric acid, lauric acid, stearic acid, behenic acid, erucic acid, oleic acid, linoleic acid, myristic acid, benzoic acid, palmitic acid, phenylacetic acid, naphthalenoic acid, dimerized derivatives thereof. Suitable organic acids are more fully described, for example, in U.S. Pat. No. 6,756,436, the entire disclosure of which is hereby incorporated herein by reference.

Additional melt flow modifiers suitable for use in compositions of the present invention, include the non-fatty acid

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melt flow modifiers described in U.S. Pat. Nos. 7,365,128 and 7,402,629, the entire disclosures of which are hereby incorporated herein by reference.

HNP outer core layer compositions of the present invention optionally include additive(s) and/or filler(s) in an amount within a range having a lower limit of 0 or 5 or 10 wt %, and an upper limit of 25 or 30 or 50 wt %, based on the total weight of the composition. Suitable additives and fillers include, but are not limited to, chemical blowing and foaming agents, optical brighteners, coloring agents, fluorescent agents, whitening agents, UV absorbers, light stabilizers, defoaming agents, processing aids, mica, talc, nano-fillers, antioxidants, stabilizers, softening agents, fragrance components, plasticizers, impact modifiers, TiO₂, acid copolymer wax, surfactants, and fillers, such as zinc oxide, tin oxide, barium sulfate, zinc sulfate, calcium oxide, calcium carbonate, zinc carbonate, barium carbonate, clay, tungsten, tungsten carbide, silica, lead silicate, regrind (recycled material), and mixtures thereof. Suitable additives are more fully described in, for example, U.S. Patent Application Publication No. 2003/0225197, the entire disclosure of which is hereby incorporated herein by reference.

In a particular embodiment, the HNP outer core layer composition has a moisture vapor transmission rate ("MVTR") of 8 g-mil/100 in²/day or less (i.e., 3.2 g-mm/m²·day or less), or 5 g-mil/100 in²/day or less (i.e., 2.0 g-mm/m²·day or less), or 3 g-mil/100 in²/day or less (i.e., 1.2 g-mm/m²·day or less), or 2 g-mil/100 in²/day or less (i.e., 0.8 g-mm/m²·day or less), or 1 g-mil/100 in²/day or less (i.e., 0.4 g-mm/m²·day or less), or less than 1 g-mil/100 in²/day (i.e., less than 0.4 g-mm/m²·day). Suitable moisture resistant HNP compositions are disclosed, for example, in U.S. Patent Application Publications Nos. 2005/0267240, 2006/0106175 and 2006/0293464, the entire disclosures of which are hereby incorporated herein by reference.

In another particular embodiment, a sphere formed from the HNP outer core layer composition has a compression of 70 or greater, or 80 or greater, or a compression within a range having a lower limit of 70 or 80 or 90 or 100 and an upper limit of 110 or 130 or 140.

HNP outer core layer compositions of the present invention are not limited by any particular method or any particular equipment for making the compositions. In a preferred embodiment, the composition is prepared by the following process. The acid polymer(s), preferably an ethylene/(meth)acrylic acid copolymer, optional melt flow modifier(s), and optional additive(s)/filler(s) are simultaneously or individually fed into a melt extruder, such as a single or twin screw extruder. A suitable amount of cation source is then added such that at least 80%, preferably at least 90%, more preferably at least 95%, and even more preferably 100%, of all acid groups present are neutralized. The acid polymer may be at least partially neutralized prior to the above process. The components are intensively mixed prior to being extruded as a strand from the die-head.

Suitable HNP outer core layer compositions of the present invention also include blends of HNPs with partially neutralized ionomers as disclosed, for example, in U.S. Patent Application Publication No. 2006/0128904, the entire disclosure of which is hereby incorporated herein by reference, and blends of HNPs with additional thermoplastic and elastomeric materials. Examples of thermoplastic materials suitable for blending include bimodal ionomers (e.g., as disclosed in U.S. Patent Application Publication No. 2004/0220343 and U.S. Pat. Nos. 6,562,906, 6,762,246 and 7,273,903, the entire disclosures of which are hereby incorporated herein by reference), ionomers modified with rosins (e.g., as disclosed in

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U.S. Patent Application Publication No. 2005/0020741, the entire disclosure of which is hereby incorporated by reference), soft and resilient ethylene copolymers (e.g., as disclosed U.S. Patent Application Publication No. 2003/0114565, the entire disclosure of which is hereby incorporated herein by reference), polyolefins, polyamides, polyesters, polyethers, polycarbonates, polysulfones, polyacetals, polylactones, acrylonitrile-butadiene-styrene resins, polyphenylene oxide, polyphenylene sulfide, styrene-acrylonitrile resins, styrene maleic anhydride, polyimides, aromatic polyketones, ionomers and ionomeric precursors, acid copolymers, conventional HNPs, polyurethanes, grafted and non-grafted metallocene-catalyzed polymers, single-site catalyst polymerized polymers, high crystalline acid polymers, cationic ionomers, and combinations thereof. Particular polyolefins suitable for blending include one or more, linear, branched, or cyclic, C₂-C₄₀ olefins, particularly polymers comprising ethylene or propylene copolymerized with one or more C₂-C₄₀ olefins, C₃-C₂₀ α-olefins, or C₃-C₁₀ α-olefins. Particular conventional HNPs suitable for blending include, but are not limited to, one or more of the HNPs disclosed in U.S. Pat. Nos. 6,756,436, 6,894,098, and 6,953,820, the entire disclosures of which are hereby incorporated herein by reference. Examples of elastomers suitable for blending include natural and synthetic rubbers, including, but not limited to, ethylene propylene rubber ("EPR"), ethylene propylene diene rubber ("EPDM"), styrenic block copolymer rubbers (such as SI, SIS, SB, SBS, SIBS, and the like, where "S" is styrene, "I" is isobutylene, and "B" is butadiene), butyl rubber, halobutyl rubber, copolymers of isobutylene and para-alkylstyrene, halogenated copolymers of isobutylene and para-alkylstyrene, natural rubber, polyisoprene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and polybutadiene rubber (cis and trans). Additional suitable blend polymers include those described in U.S. Pat. No. 5,981,658, for example at column 14, lines 30 to 56, the entire disclosure of which is hereby incorporated herein by reference. The blends described herein may be produced by post-reactor blending, by connecting reactors in series to make reactor blends, or by using more than one catalyst in the same reactor to produce multiple species of polymer. The polymers may be mixed prior to being put into an extruder, or they may be mixed in an extruder.

HNP outer core layer compositions of the present invention, in the neat (i.e., unfilled) form, preferably have a specific gravity of from 0.95 g/cc to 0.99 g/cc. Any suitable filler, flake, fiber, particle, or the like, of an organic or inorganic material may be added to the HNP composition to increase or decrease the specific gravity, particularly to adjust the weight distribution within the golf ball, as further disclosed in U.S. Pat. Nos. 6,494,795, 6,547,677, 6,743,123, 7,074,137, and 6,688,991, the entire disclosures of which are hereby incorporated herein by reference.

Suitable HNP compositions are further disclosed, for example, in U.S. Pat. Nos. 6,653,382, 6,756,436, 6,777,472, 6,894,098, 6,919,393, and 6,953,820, the entire disclosures of which are hereby incorporated herein by reference.

Particularly suitable for use in forming outer core layers of golf balls of the present invention are the "relatively hard HNP compositions" disclosed in U.S. Patent Application Publication No. 2007/0207879, the "high modulus HNP compositions" disclosed in U.S. Pat. No. 7,207,903, and the highly neutralized acid polymer compositions disclosed in U.S. Pat. No. 6,994,638, the entire disclosures of which are hereby incorporated herein by reference.

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The outer core layer is alternatively formed from a highly resilient thermoplastic polymer composition selected from Hytrel® thermoplastic polyester elastomers, commercially available from E. I. du Pont de Nemours and Company, and Pebax® thermoplastic polyether block amides, commercially available from Arkema Inc.

Additional materials suitable for forming the inner and outer core layers include the core compositions disclosed in U.S. Pat. No. 7,300,364, the entire disclosure of which is hereby incorporated herein by reference. For example, suitable core materials include HNPs neutralized with organic fatty acids and salts thereof, metal cations, or a combination of both. In addition to HNPs neutralized with organic fatty acids and salts thereof, core compositions may comprise at least one rubber material having a resilience index of at least about 40. Preferably the resilience index is at least about 50.

The weight distribution of the cores disclosed herein can be varied to achieve certain desired parameters, such as spin rate, compression, and initial velocity.

The two-layer core is enclosed with a cover comprising an inner cover layer and an outer cover layer. According to the present invention, the surface hardness of the outer core layer's outer surface is greater than the material hardness of the inner cover layer. In a particular embodiment, the surface hardness of the outer core layer's outer surface is greater than the material hardness of both the inner cover layer and the outer cover layer.

It should be understood that there is a fundamental difference between "material hardness" and "hardness as measured directly on a golf ball." For purposes of the present disclosure, material hardness is measured according to ASTM D2240 and generally involves measuring the hardness of a flat "slab" or "button" formed of the material. Hardness as measured directly on a golf ball (or other spherical surface) typically results in a different hardness value. This difference in hardness values is due to several factors including, but not limited to, ball construction (i.e., core type, number of core and/or cover layers, etc.), ball (or sphere) diameter, and the material composition of adjacent layers. It should also be understood that the two measurement techniques are not linearly related and, therefore, one hardness value cannot easily be correlated to the other. Unless otherwise stated, the material hardness values given herein for cover materials are measured according to ASTM D2240, with all values reported following 10 days of aging at 50% relative humidity and 23° C.

The inner cover layer preferably has an outer surface hardness of 95 Shore C or less, or an outer surface hardness within a range having a lower limit of 80 or 85 or 87 Shore C and an upper limit of 90 or 91 or 95 Shore C. For purposes of the present disclosure, the outer surface hardness of the inner cover layer is measured according to the procedure given herein for measuring the outer surface hardness of a golf ball layer.

The inner cover layer preferably has a material hardness ($H_{\text{inner cover}}$) of 95 Shore C or less, or less than 95 Shore C, or 92 Shore C or less, or 90 Shore C or less, or has a material hardness ($H_{\text{inner cover}}$) within a range having a lower limit of 70 or 75 or 80 or 84 or 85 or 87 Shore C and an upper limit of 90 or 91 or 92 or 95 Shore C. The thickness of the inner cover layer is preferably within a range having a lower limit of 0.010 or 0.015 or 0.020 or 0.025 or 0.030 inches and an upper limit of 0.035 or 0.045 or 0.050 or 0.080 or 0.120 or 0.150 inches.

The outer cover layer preferably has an outer surface hardness within a range having a lower limit of 20 or 30 or 35 or 40 Shore D and an upper limit of 52 or 58 or 60 or 65 or 70 or 72 or 75 Shore D.

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The outer cover layer preferably has a material hardness of 85 Shore C or less. The thickness of the outer cover layer is preferably within a range having a lower limit of 0.010 or 0.015 or 0.020 or 0.025 inches and an upper limit of 0.035 or 0.040 or 0.050 or 0.055 or 0.080 inches.

Optional intermediate cover layers may be included and generally have a thickness within a range having a lower limit of 0.010 or 0.020 or 0.025 inches and an upper limit of 0.050 or 0.150 or 0.200 inches.

The cover preferably has an overall thickness within a range having a lower limit of 0.010 or 0.020 or 0.025 or 0.030 or 0.040 or 0.045 or 0.050 or 0.060 inches and an upper limit of 0.070 or 0.075 or 0.080 or 0.090 or 0.100 or 0.150 or 0.200 or 0.300 or 0.500 inches.

Cover materials are preferably cut-resistant materials, selected based on the desired performance characteristics. Suitable inner and outer cover layer materials for the golf balls disclosed herein include, but are not limited to, ionomer resins and blends thereof (e.g., Surlyn® ionomer resins and DuPont® HPF 1000 and HPF 2000, commercially available from E. I. du Pont de Nemours and Company; Iotek® ionomers, commercially available from ExxonMobil Chemical Company; Amplify® JO ionomers of ethylene acrylic acid copolymers, commercially available from The Dow Chemical Company; and Clarix® ionomer resins, commercially available from A. Schulman Inc.); polyurethanes; polyureas; copolymers and hybrids of polyurethane and polyurea; polyethylene, including, for example, low density polyethylene, linear low density polyethylene, and high density polyethylene; polypropylene; rubber-toughened olefin polymers; acid copolymers, e.g., (meth)acrylic acid, which do not become part of an ionomeric copolymer; plastomers; flexomers; styrene/butadiene/styrene block copolymers; styrene/ethylene/butylene/styrene block copolymers; dynamically vulcanized elastomers; ethylene vinyl acetates; ethylene methyl acrylates; polyvinyl chloride resins; polyamides, amide-ester elastomers, and graft copolymers of ionomer and polyamide, including, for example, Pebax® thermoplastic polyether block amides, commercially available from Arkema Inc; crosslinked trans-polyisoprene and blends thereof; polyester-based thermoplastic elastomers, such as Hytrel®, commercially available from E. I. du Pont de Nemours and Company; polyurethane-based thermoplastic elastomers, such as Elastollan®, commercially available from BASF; synthetic or natural vulcanized rubber; and combinations thereof. Suitable cover materials and constructions also include, but are not limited to, those disclosed in U.S. Pat. Nos. 6,117,025, 6,767,940, and 6,960,630, the entire disclosures of which are hereby incorporated herein by reference.

Compositions comprising an ionomer or a blend of two or more ionomers are particularly suitable for forming the inner cover layer in dual-layer covers. Preferred ionomeric compositions include:

- (a) a composition comprising a "high acid ionomer" (i.e., having an acid content of greater than 16 wt %), such as Surlyn 8150®, a copolymer of ethylene and methacrylic acid, having an acid content of 19 wt %, which is 45% neutralized with sodium;
- (b) a composition comprising a high acid ionomer and a maleic anhydride-grafted non-ionomeric polymer (e.g., Fusabond® maleic anhydride-grafted metallocene-catalyzed ethylene-butene copolymers). A particularly preferred blend of high acid ionomer and maleic anhydride-grafted polymer is a blend of 79-85 wt % Surlyn 8150® and 15-21 wt % Fusabond®. Blends of high acid ionomers with maleic anhydride-grafted polymers are further disclosed, for example, in U.S. Pat. Nos. 6,992,

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- 135 and 6,677,401, the entire disclosures of which are hereby incorporated herein by reference;
- (c) a composition comprising a 50/45/5 blend of Surlyn® 8940/Surlyn® 9650/Nucel® 960, preferably having a material hardness of from 80 to 85 Shore C;
 - (d) a composition comprising a 50/25/25 blend of Surlyn® 8940/Surlyn® 9650/Surlyn® 9910, preferably having a material hardness of about 90 Shore C;
 - (e) a composition comprising a 50/50 blend of Surlyn® 8940/Surlyn® 9650, preferably having a material hardness of about 86 Shore C;
 - (f) a composition comprising a blend of Surlyn® 7940/Surlyn® 8940, optionally including a melt flow modifier;
 - (g) a composition comprising a blend of a first high acid ionomer and a second high acid ionomer, wherein the first high acid ionomer is neutralized with a different cation than the second high acid ionomer (e.g., 50/50 blend of Surlyn® 8150 and Surlyn® 9150), optionally including one or more melt flow modifiers such as an ionomer, ethylene-acid copolymer or ester terpolymer; and
 - (h) a composition comprising a blend of a first high acid ionomer and a second high acid ionomer, wherein the first high acid ionomer is neutralized with a different cation than the second high acid ionomer, and from 0 to 10 wt % of an ethylene/acid/ester ionomer wherein the ethylene/acid/ester ionomer is neutralized with the same cation as either the first high acid ionomer or the second high acid ionomer or a different cation than the first and second high acid ionomers (e.g., a blend of 40-50 wt % Surlyn® 8140, 40-50 wt % Surlyn® 9120, and 0-10 wt % Surlyn® 6320).

Surlyn® 8150®, Surlyn® 8940, and Surlyn® 8140 are different grades of E/MAA copolymer in which the acid groups have been partially neutralized with sodium ions. Surlyn® 9650, Surlyn® 9910, Surlyn® 9150, and Surlyn® 9120 are different grades of E/MAA copolymer in which the acid groups have been partially neutralized with zinc ions. Surlyn® 7940 is an E/MAA copolymer in which the acid groups have been partially neutralized with lithium ions. Surlyn® 6320 is a very low modulus magnesium ionomer with a medium acid content. Nucel® 960 is an E/MAA copolymer resin nominally made with 15 wt % methacrylic acid. Surlyn® ionomers, Fusabond® copolymers, and Nucel® copolymers are commercially available from E. I. du Pont de Nemours and Company.

Non-limiting examples of particularly preferred ionomeric cover layer formulations are shown in Table 1 below.

TABLE 1

Cover Layer Material	Surlyn® 8150, wt %	Fusabond®, wt %	Shore C Hardness*
1	89	11	91.2
2	84	16	89.8
3	84	16	90.4
4	84	16	89.6
5	81	19	88.9
6	80	20	89.1
7	78	22	88.1
8	76	24	87.6
9	76	24	87.2
10	73	27	86.6
11	71	29	86.7
12	67	33	84.0

*Flex bars of each blend composition were formed and evaluated for hardness according to ASTM D2240 following 10 days of aging at 50% relative humidity and 23° C.

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Ionomeric cover compositions can be blended with non-ionic thermoplastic resins, particularly to manipulate product properties. Examples of suitable non-ionic thermoplastic resins include, but are not limited to, polyurethane, poly-ether-ester, poly-amide-ether, polyether-urea, thermoplastic poly-ether block amides (e.g., Pebax® block copolymers, commercially available from Arkema Inc.), styrene-butadiene-styrene block copolymers, styrene(ethylene-butylene)-styrene block copolymers, polyamides, polyesters, polyolefins (e.g., polyethylene, polypropylene, ethylene-propylene copolymers, polyethylene-(meth)acrylate, polyethylene-(meth)acrylic acid, functionalized polymers with maleic anhydride grafting, Fusabond® functionalized olefins commercially available from E. I. du Pont de Nemours and Company, functionalized polymers with epoxidation, elastomers (e.g., ethylene propylene diene monomer rubber, metallocene-catalyzed polyolefin) and ground powders of thermoset elastomers.

Suitable ionomeric cover materials are further disclosed, for example, in U.S. Pat. Nos. 6,653,382, 6,756,436, 6,894,098, 6,919,393, and 6,953,820, the entire disclosures of which are hereby incorporated by reference.

Polyurethanes, polyureas, and copolymers and blends thereof are particularly suitable for forming the outer cover layer in dual-layer covers. When used as cover layer materials, polyurethanes and polyureas can be thermoset or thermoplastic. Thermoset materials can be formed into golf ball layers by conventional casting or reaction injection molding techniques. Thermoplastic materials can be formed into golf ball layers by conventional compression or injection molding techniques.

Suitable polyurethane cover materials are further disclosed in U.S. Pat. Nos. 5,334,673, 6,506,851, 6,756,436, and 7,105,623, the entire disclosures of which are hereby incorporated herein by reference. Suitable polyurea cover materials are further disclosed in U.S. Pat. Nos. 5,484,870, 6,835,794 and 7,378,483, and U.S. Patent Application Publication No. 2008/0064527, the entire disclosures of which are hereby incorporated herein by reference. Suitable polyurethane-urea cover materials include polyurethane/polyurea blends and copolymers comprising urethane and urea segments, as disclosed in U.S. Patent Application Publication No. 2007/0117923, the entire disclosure of which is hereby incorporated herein by reference.

Golf ball cover compositions may include a flow modifier, such as, but not limited to, Nucel® acid copolymer resins, and particularly Nucel® 960. Nucel® acid copolymer resins are commercially available from E. I. du Pont de Nemours and Company.

Cover compositions may also include one or more filler(s), such as the fillers given above for rubber compositions of the present invention (e.g., titanium dioxide, barium sulfate, etc.), and/or additive(s), such as coloring agents, fluorescent agents, whitening agents, antioxidants, dispersants, UV absorbers, light stabilizers, plasticizers, surfactants, compatibility agents, foaming agents, reinforcing agents, release agents, and the like.

In a particular embodiment, the cover comprises an inner cover layer formed from a composition comprising a high acid ionomer and a maleic anhydride-grafted non-ionic polyurethane and an outer cover layer formed from a polyurethane, polyurea, or copolymer or hybrid of polyurethane/polyurea. The outer cover layer material may be thermoplastic or thermoset. A particularly preferred inner cover layer composition is a 84 wt %/16 wt % blend of Surlyn® 8150® and Fusabond 572D®.

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Additional suitable cover materials are disclosed, for example, in U.S. Patent Application Publication No. 2005/0164810, U.S. Pat. No. 5,919,100, and PCT Publications WO00/23519 and WO00/29129, the entire disclosures of which are hereby incorporated herein by reference.

Golf balls of the present invention optionally include one or more intermediate layer(s) disposed between the core and the cover. When present, the overall thickness of the intermediate layer(s) is generally within a range having a lower limit of 0.010 or 0.050 or 0.100 inches and an upper limit of 0.300 or 0.350 or 0.400 inches. Suitable intermediate layer materials include, but are not limited to, natural rubbers, balata, gutta-percha, cis-polybutadienes, trans-polybutadienes, synthetic polyisoprene rubbers, polyoctenamers, styrene-propylene-diene rubbers, metallocene rubbers, styrene-butadiene rubbers, ethylene-propylene rubbers, chloroprene rubbers, acrylonitrile rubbers, acrylonitrile-butadiene rubbers, styrene-ethylene block copolymers, maleic anhydride or succinate modified metallocene catalyzed ethylene copolymers, polypropylene resins, ionomer resins, polyamides, polyesters, polyurethanes, polyureas, chlorinated polyethylenes, polysulfide rubbers, fluorocarbons, and combinations thereof.

A moisture vapor barrier layer is optionally employed between the core and the cover. Moisture vapor barrier layers are further disclosed, for example, in U.S. Pat. Nos. 6,632, 147, 6,932,720, 7,004,854, and 7,182,702, the entire disclosures of which are hereby incorporated herein by reference.

In addition to the material disclosed above, any of the core or cover layers may comprise one or more of the following materials: thermoplastic elastomer, thermoset elastomer, synthetic rubber, thermoplastic vulcanizate, copolymeric ionomer, terpolymeric ionomer, polycarbonate, polyolefin, polyamide, copolymeric polyamide, polyesters, polyester-amides, polyether-amides, polyvinyl alcohols, acrylonitrile-butadiene-styrene copolymers, polyarylate, polyacrylate, polyphenylene ether, impact-modified polyphenylene ether, high impact polystyrene, diallyl phthalate polymer, metallocene-catalyzed polymers, styrene-acrylonitrile (SAN), olefin-modified SAN, acrylonitrile-styrene-acrylonitrile, styrene-maleic anhydride (S/MA) polymer, styrenic copolymer, functionalized styrenic copolymer, functionalized styrenic terpolymer, styrenic terpolymer, cellulose polymer, liquid crystal polymer (LCP), ethylene-propylene-diene rubber (EPDM), ethylene-vinyl acetate copolymer (EVA), ethylene propylene rubber (EPR), ethylene vinyl acetate, polyurea, and polysiloxane. Suitable polyamides for use as an additional material in compositions disclosed herein also include resins obtained by: (1) polycondensation of (a) a dicarboxylic acid, such as oxalic acid, adipic acid, sebacic acid, terephthalic acid, isophthalic acid or 1,4-cyclohexanedicarboxylic acid, with (b) a diamine, such as ethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, or decamethylenediamine, 1,4-cyclohexyldiamine or m-xylylenediamine; (2) a ring-opening polymerization of cyclic lactam, such as ϵ -caprolactam or ω -lauro lactam; (3) polycondensation of an aminocarboxylic acid, such as 6-aminocaproic acid, 9-aminononanoic acid, 11-aminoundecanoic acid or 12-aminododecanoic acid; or (4) copolymerization of a cyclic lactam with a dicarboxylic acid and a diamine. Specific examples of suitable polyamides include Nylon 6, Nylon 66, Nylon 610, Nylon 11, Nylon 12, copolymerized Nylon, Nylon MXD6, and Nylon 46.

Other preferred materials suitable for use as an additional material in golf ball compositions disclosed herein include Skypel polyester elastomers, commercially available from SK Chemicals of South Korea; Septon® diblock and triblock

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copolymers, commercially available from Kuraray Corporation of Kurashiki, Japan; and Kraton® diblock and triblock copolymers, commercially available from Kraton Polymers LLC of Houston, Tex.

Compositions disclosed herein can be either foamed or filled with density adjusting materials to provide desirable golf ball performance characteristics.

The present invention is not limited by any particular process for forming the golf ball layer(s). It should be understood that the layer(s) can be formed by any suitable technique, including injection molding, compression molding, casting, and reaction injection molding.

When injection molding is used, the composition is typically in a pelletized or granulated form that can be easily fed into the throat of an injection molding machine wherein it is melted and conveyed via a screw in a heated barrel at temperatures of from 150° F. to 600° F., preferably from 200° F. to 500° F. The molten composition is ultimately injected into a closed mold cavity, which may be cooled, at ambient or at an elevated temperature, but typically the mold is cooled to a temperature of from 50° F. to 70° F. After residing in the closed mold for a time of from 1 second to 300 seconds, preferably from 20 seconds to 120 seconds, the core and/or core plus one or more additional core or cover layers is removed from the mold and either allowed to cool at ambient or reduced temperatures or is placed in a cooling fluid such as water, ice water, dry ice in a solvent, or the like.

When compression molding is used to form a core, the composition is first formed into a preform or slug of material, typically in a cylindrical or roughly spherical shape at a weight slightly greater than the desired weight of the molded core. Prior to this step, the composition may be first extruded or otherwise melted and forced through a die after which it is cut into a cylindrical preform. The preform is then placed into a compression mold cavity and compressed at a mold temperature of from 150° F. to 400° F., preferably from 250° F. to 400° F., and more preferably from 300° F. to 400° F. When compression molding a cover layer, half-shells of the cover layer material are first formed via injection molding. A core is then enclosed within two half-shells, which is then placed into a compression mold cavity and compressed.

Reaction injection molding processes are further disclosed, for example, in U.S. Pat. Nos. 6,083,119, 7,208,562, 7,281,997, 7,282,169, 7,338,391, and U.S. Patent Application Publication No. 2006/0247073, the entire disclosures of which are hereby incorporated herein by reference.

Golf balls of the present invention typically have a coefficient of restitution ("COR") of 0.700 or greater, preferably 0.750 or greater, more preferably 0.780 or greater, and even more preferably 0.790 or greater.

COR, as used herein, is determined according to a known procedure wherein a golf ball or golf ball subassembly (e.g., a golf ball core) is fired from an air cannon at two given velocities and calculated at a velocity of 125 ft/s. Ballistic light screens are located between the air cannon and the steel plate at a fixed distance to measure ball velocity. As the ball travels toward the steel plate, it activates each light screen, and the time at each light screen is measured. This provides an incoming transit time period inversely proportional to the ball's incoming velocity. The ball impacts the steel plate and rebounds through the light screens, which again measure the time period required to transit between the light screens. This provides an outgoing transit time period inversely proportional to the ball's outgoing velocity. COR is then calculated as the ratio of the outgoing transit time period to the incoming transit time period, $COR = V_{out}/V_{in} = T_{in}/T_{out}$.

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Golf balls of the present invention typically have an overall compression of 40 or greater, or a compression within a range having a lower limit of 40 or 50 or 60 or 65 or 75 or 80 or 90 and an upper limit of 95 or 100 or 105 or 110 or 115 or 120. Dual cores of the present invention preferably have an overall compression of 60 or 70 or 75 or 80 and an upper limit of 85 or 90 or 95 or 100. Inner core layers of the present invention preferably have a compression of 40 or less, or from 20 to 40, or a compression of about 35.

Compression is an important factor in golf ball design. For example, the compression of the core can affect the ball's spin rate off the driver and the feel. As disclosed in Jeff Dalton's *Compression by Any Other Name, Science and Golf IV, Proceedings of the World Scientific Congress of Golf* (Eric Thain ed., Routledge, 2002) ("J. Dalton"), several different methods can be used to measure compression, including Atti compression, Riehle compression, load/deflection measurements at a variety of fixed loads and offsets, and effective modulus. For purposes of the present invention, "compression" refers to Atti compression and is measured according to a known procedure, using an Atti compression test device, wherein a piston is used to compress a ball against a spring. The travel of the piston is fixed and the deflection of the spring is measured. The measurement of the deflection of the spring does not begin with its contact with the ball; rather, there is an offset of approximately the first 1.25 mm (0.05 inches) of the spring's deflection. Very low stiffness cores will not cause the spring to deflect by more than 1.25 mm and therefore have a zero compression measurement. The Atti compression tester is designed to measure objects having a diameter of 42.7 mm (1.68 inches); thus, smaller objects, such as golf ball cores, must be shimmed to a total height of 42.7 mm to obtain an accurate reading. Conversion from Atti compression to Riehle (cores), Riehle (balls), 100 kg deflection, 130-10 kg deflection or effective modulus can be carried out according to the formulas given in J. Dalton.

Golf balls of the present invention will typically have dimple coverage of 60% or greater, preferably 65% or greater, and more preferably 75% or greater.

The United States Golf Association specifications limit the minimum size of a competition golf ball to 1.680 inches. There is no specification as to the maximum diameter, and golf balls of any size can be used for recreational play. Golf balls of the present invention can have an overall diameter of any size. The preferred diameter of the present golf balls is from 1.680 inches to 1.800 inches. More preferably, the present golf balls have an overall diameter of from 1.680 inches to 1.760 inches, and even more preferably from 1.680 inches to 1.740 inches.

Golf balls of the present invention preferably have a moment of inertia ("MOI") of 70-95 g·cm², preferably 75-93 g·cm², and more preferably 76-90 g·cm². For low MOI embodiments, the golf ball preferably has an MOI of 85 g·cm² or less, or 83 g·cm² or less. For high MOI embodiment, the golf ball preferably has an MOI of 86 g·cm² or greater, or 87 g·cm² or greater. MOI is measured on a model MOI-005-104 Moment of Inertia Instrument manufactured by Inertia Dynamics of Collinsville, Conn. The instrument is connected to a PC for communication via a COMM port and is driven by MOI Instrument Software version #1.2.

When numerical lower limits and numerical upper limits are set forth herein, it is contemplated that any combination of these values may be used.

All patents, publications, test procedures, and other references cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not

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inconsistent with this invention and for all jurisdictions in which such incorporation is permitted.

While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those of ordinary skill in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein, but rather that the claims be construed as encompassing all of the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those of ordinary skill in the art to which the invention pertains.

What is claimed is:

1. A golf ball consisting essentially of:

an inner core layer formed from a rubber composition and having a diameter of from about 0.75 inches to about 1.4 inches, a center hardness (H_{center}) of about 40 Shore C or greater, and an outer surface hardness of 60 Shore C or greater;

an outer core layer having a diameter of about 1.4 inches to about 1.55 inches formed from a highly neutralized polymer composition and having an outer surface hardness ($H_{outer\ core}$) of about 80 Shore C or greater;

an inner cover layer formed from a thermoplastic composition and having a material hardness ($H_{inner\ cover}$) less than the outer surface hardness of the outer core layer; and

an outer cover layer formed from a composition selected from the group consisting of polyurethanes, polyureas, and copolymers and blends thereof.

2. The golf ball of claim 1, wherein $H_{outer\ core} - H_{center} \geq 20$ Shore C units.

3. The golf ball of claim 1, wherein $H_{outer\ core} - H_{center} \geq 30$ Shore C units.

4. The golf ball of claim 1, wherein H_{center} is from about 50 Shore C to about 80 Shore C.

5. The golf ball of claim 1, wherein the outer surface hardness of the inner core layer is from about 65 Shore C to about 90 Shore C.

6. The golf ball of claim 1, wherein the outer surface hardness of the inner core layer is from about 70 Shore C to about 85 Shore C.

7. The golf ball of claim 1, wherein $H_{outer\ core}$ is about 90 Shore C or greater.

8. The golf ball of claim 1, wherein $H_{outer\ core}$ is greater than about 85 Shore C, and wherein $H_{inner\ cover}$ is from about 80 Shore C to about 85 Shore C.

9. The golf ball of claim 1, wherein $H_{outer\ core}$ is 85 Shore C or greater, and wherein $H_{inner\ cover}$ is from 84 Shore C to 92 Shore C.

10. The golf ball of claim 1, wherein H_{center} is from about 55 Shore C to about 75 Shore C, the outer surface hardness of the inner core layer is from about 75 Shore C to about 90 Shore C, and $H_{outer\ core}$ is greater than about 85 Shore C.

11. The golf ball of claim 10, wherein $H_{inner\ cover}$ is from about 80 Shore C to about 85 Shore C.

12. The golf ball of claim 10, wherein $H_{outer\ core}$ is greater than 87 Shore C, and wherein $H_{inner\ cover}$ is from about 80 Shore C to about 85 Shore C.

13. The golf ball of claim 12, wherein $H_{outer\ core}$ is about 90 Shore C or greater.

14. The golf ball of claim 1, wherein the inner core layer has a compression of about 40 or less.

15. The golf ball of claim 14, wherein the core has an overall dual core compression of from about 60 to about 95.

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16. The golf ball of claim 1, wherein the core has an overall dual core diameter of from about 1.5 inches to about 1.55 inches.

17. A golf ball consisting essentially of:

an inner core layer formed from a rubber composition and having a diameter of from about 0.75 inches to about 1.4 inches, a center hardness (H_{center}) of about 50 Shore C or greater, and an outer surface hardness of about 65 Shore C or greater;

an outer core layer having an outer diameter of about 1.4 to about 1.59 formed from a highly neutralized polymer composition and having an outer surface hardness ($H_{outer\ core}$) of about 75 Shore C or greater;

an inner cover layer formed from a thermoplastic composition and having a material hardness ($H_{inner\ cover}$) of from about 75 Shore C to about 95 Shore C; and

an outer cover layer formed from a composition selected from the group consisting of polyurethanes, polyureas, and copolymers and blends thereof.

18. The golf ball of claim 17, wherein $H_{outer\ core} - H_{center} \geq 20$ Shore C units.

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19. The golf ball of claim 17, wherein $H_{outer\ core} - H_{center} \geq 25$ Shore C units.

20. A golf ball comprising:

a core consisting of:

an inner core layer formed from a rubber composition and having a diameter of from about 0.75 inches to about 1.35 inches, a center hardness (H_{center}) of from about 50 Shore C to about 75 Shore C, and an outer surface hardness of from about 60 Shore C to about 85 Shore C; and

an outer core layer formed from a highly neutralized polymer composition and having an outer surface hardness ($H_{outer\ core}$) of from about 80 Shore C to about 90 Shore C; and

a cover consisting of:

an inner cover layer formed from a thermoplastic composition and having a material hardness ($H_{inner\ cover}$) of from about 75 Shore C to about 85 Shore C; and

an outer cover layer formed from a composition selected from the group consisting of polyurethanes, polyureas, and copolymers and blends thereof.

* * * * *

Exhibit F

(12) **United States Patent**
Sullivan et al.(10) **Patent No.:** **US 9,320,944 B2**(45) **Date of Patent:** **Apr. 26, 2016**(54) **MULTI-LAYER COVER DUAL CORE GOLF BALL HAVING A HIGH ACID CASING AND LOW GRADIENT CENTER**(71) Applicant: **Acushnet Company**, Fairhaven, MA (US)(72) Inventors: **Michael J. Sullivan**, Old Lyme, CT (US); **Brian Comeau**, Berkley, MA (US); **Scott Cooper**, Warwick, RI (US); **Douglas E. Jones**, Dartmouth, MA (US); **Derek A. Ladd**, Acushnet, MA (US)(73) Assignee: **Acushnet Company**, Fairhaven, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/144,463**(22) Filed: **Dec. 30, 2013**(65) **Prior Publication Data**

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Related U.S. Application Data

(63) Continuation-in-part of application No. 13/723,469, filed on Dec. 21, 2012, now Pat. No. 8,845,456, which is a continuation of application No. 13/438,947, filed on Apr. 4, 2012, now Pat. No. 8,337,330, which is a continuation of application No. 12/964,343, filed on Dec. 9, 2010, now Pat. No. 8,152,655, which is a

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A63B 37/00 (2006.01)
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(Continued)

(58) **Field of Classification Search**CPC **A63B 37/0063**
USPC **473/373, 374**
See application file for complete search history.(56) **References Cited**

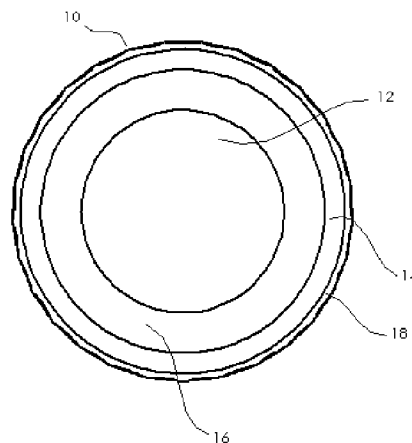
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Primary Examiner — Raeann Gorden(74) *Attorney, Agent, or Firm* — William B. Lacy(57) **ABSTRACT**

A golf ball having an inner core layer having an outer surface and a geometric center and being formed from a rubber composition. An outer core layer surrounds the inner core to form a dual core. An inner cover layer surrounds the dual core, and includes a high-acid ionomer having a hardness of about 66 to 75 Shore D and an acid content of 16 wt. % or greater. An outer cover layer surrounds the inner cover layer, and includes a polyurethane and having a material hardness of about 38 to 56 Shore D. The inner core layer surface hardness is from 0 Shore C to 10 Shore C lower than the geometric center hardness to define a negative hardness gradient and the outer core layer has a surface hardness at least 10 Shore C greater than the geometric center hardness to define a dual core positive hardness gradient.

9 Claims, 2 Drawing Sheets

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Related U.S. Application Data

continuation-in-part of application No. 12/647,584, filed on Dec. 28, 2009, now Pat. No. 8,500,575, which is a continuation-in-part of application No. 12/558,826, filed on Sep. 14, 2009, now Pat. No. 7,857,714, which is a continuation of application No. 12/186,877, filed on Aug. 6, 2008, now Pat. No. 7,803,069, which is a continuation of application No. 11/832,197, filed on Aug. 1, 2007, now Pat. No. 7,410,429, which is a continuation-in-part of application No. 11/829,461, filed on Jul. 27, 2007, now Pat. No. 7,537,530, which is a continuation-in-part of application No. 11/772,903, filed on Jul. 3, 2007, now Pat. No. 7,537,529.

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C08L 23/08 (2006.01)
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CPC ... *B32B2307/536* (2013.01); *B32B 2307/7246*
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75/04 (2013.01)

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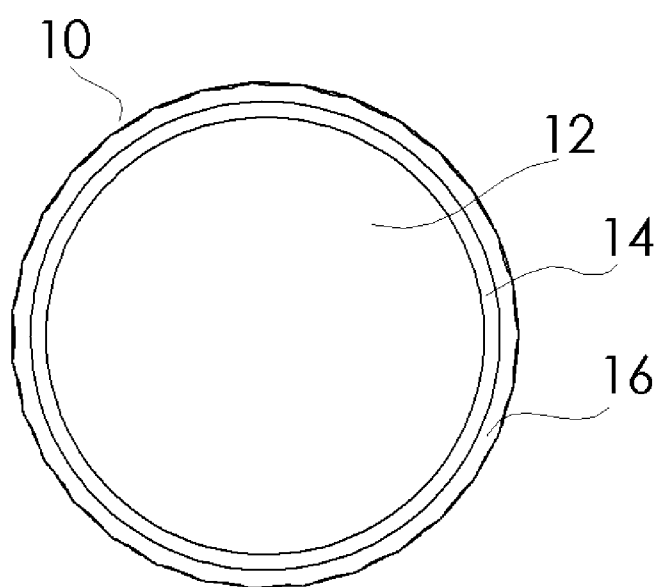


FIG. 1

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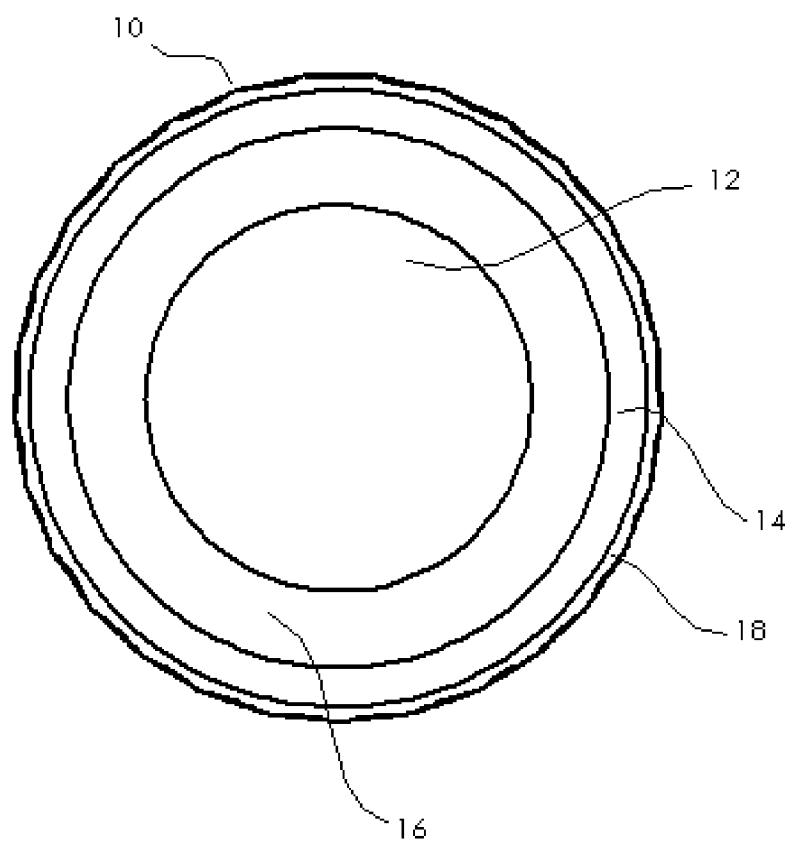


FIGURE 2

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MULTI-LAYER COVER DUAL CORE GOLF BALL HAVING A HIGH ACID CASING AND LOW GRADIENT CENTER

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of co-pending U.S. patent application Ser. No. 13/723,469, filed Dec. 21, 2012, which is a continuation of U.S. patent application Ser. No. 13/438,947, filed Apr. 4, 2012 and now U.S. Pat. No. 8,337,330, which is a continuation of U.S. patent application Ser. No. 12/964,343, filed Dec. 9, 2010 and now U.S. Pat. No. 8,152,655, which is a continuation-in-part of U.S. patent application Ser. No. 12/647,584, filed Dec. 28, 2009 and now U.S. Pat. No. 8,500,575, which is a continuation-in-part of U.S. patent application Ser. No. 12/558,826, filed Sep. 14, 2009 and now U.S. Pat. No. 7,857,714, which is a continuation of U.S. patent application Ser. No. 12/186,877, filed Aug. 6, 2008 and now U.S. Pat. No. 7,803,069, which is a continuation of U.S. patent application Ser. No. 11/832,197, filed Aug. 1, 2007 and now U.S. Pat. No. 7,410,429, which is a continuation-in-part of U.S. patent application Ser. No. 11/829,461, filed Jul. 27, 2007 and now U.S. Pat. No. 7,537,530, which is a continuation-in-part of U.S. patent application Ser. No. 11/772,903, filed Jul. 3, 2007 and now U.S. Pat. No. 7,537,529, the disclosures of which are incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates generally to golf balls with cores having one or more layers, any of the layers having a 'negative' or 'positive' hardness gradient, trans gradient, or both. More particularly, the golf ball has a core of one or more layers where at least one layer, preferably a single, solid core, has a low, "positive" hardness gradient and concurrently includes a trans-polybutadiene gradient.

BACKGROUND OF THE INVENTION

Solid golf balls are typically made with a solid core encased by a cover, both of which can have multiple layers, such as a dual core having a solid center and an outer core layer, or a multi-layer cover having an inner. Generally, golf ball cores and/or centers are constructed with a thermoset rubber, typically a polybutadiene-based composition. The cores are usually heated and crosslinked to create certain characteristics, such as higher or lower compression, which can impact the spin rate of the ball and/or provide better "feel." These and other characteristics can be tailored to the needs of golfers of different abilities. From the perspective of a golf ball manufacturer, it is desirable to have cores exhibiting a wide range of properties, such as resilience, durability, spin, and "feel," because this enables the manufacturer to make and sell many different types of golf balls suited to differing levels of ability.

Heretofore, most single core golf ball cores have had a conventional hard-to-soft hardness gradient from the surface of the core to the center of the core, otherwise known as a "positive hardness gradient." These gradients, however, are typically quite large, upwards of 15, 20, even 25 or more Shore C hardness points. The patent literature contains a number of references, additionally, that discuss a hard-surface-to-soft-center hardness gradient across a golf ball core.

U.S. Pat. No. 4,650,193 to Molitor et al. generally discloses a hardness gradient in the surface layers of a core by surface

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treating a slug of curable elastomer with a cure-altering agent and subsequently molding the slug into a core. This treatment allegedly creates a core with two zones of different compositions, the first part being the hard, resilient, central portion of the core, which was left untreated, and the second being the soft, deformable, outer layer of the core, which was treated by the cure-altering agent. The two "layers" or regions of the core are integral with one another and, as a result, achieve the effect of a gradient of soft surface to hard center.

U.S. Pat. No. 3,784,209 to Berman, et al. generally discloses a soft-to-hard hardness gradient. The '209 patent discloses a non-homogenous, molded golf ball with a core of "mixed" elastomers. A center sphere of uncured elastomeric material is surrounded by a compatible but different uncured elastomer. When both layers of elastomer are concurrently exposed to a curing agent, they become integral with one another, thereby forming a mixed core. The center of this core, having a higher concentration of the first elastomeric material, is harder than the outer layer. One drawback to this method of manufacture is the time-consuming process of creating first elastomer and then a second elastomer and then molding the two together.

Other patents discuss cores that receive a surface treatment to provide a soft 'skin'. However, since the interior portions of these cores are untreated, they have the similar hard surface to soft center gradient as conventional cores. For example, U.S. Pat. No. 6,113,831 to Nesbitt et al. generally discloses a conventional core and a separate soft skin wrapped around the core. This soft skin is created by exposing the preform slug to steam during the molding process so that a maximum mold temperature exceeds a steam set point, and by controlling exothermic molding temperatures during molding. The skin comprises the radially-outermost $\frac{1}{32}$ inch to $\frac{1}{4}$ inch of the spherical core. U.S. Pat. Nos. 5,976,443 and 5,733,206, both to Nesbitt et al., disclose the addition of water mist to the outside surface of the slug before molding in order to create a soft skin. The water allegedly softens the compression of the core by retarding crosslinking on the core surface, thereby creating an even softer soft skin around the hard central portion.

Additionally, a number of patents disclose multi-layer golf ball cores, where each core layer has a different hardness thereby creating a hardness gradient from core layer to core layer.

There remains a need, however, for a multi-layer golf ball having single layer core that has a shallow hard-to-soft ("positive") hardness gradient, from the surface to the center, and to achieve a method of producing such a core that is inexpensive and efficient.

SUMMARY OF THE INVENTION

The present invention is directed to a golf ball including a single core and a double cover. The single core has an outer surface and a geometric center, and is formed from a substantially homogenous rubber composition. The double cover includes an inner cover layer and an outer cover layer. The inner cover layer, which is disposed about the core, is formed from an ionomeric material. The inner cover layer has a material hardness of about 60 Shore D or greater. The outer cover layer is disposed about the inner cover layer and is typically formed from a castable polyurea or a castable polyurethane. This layer has a material hardness of about 60 Shore D or less. In one preferred embodiment, the outer surface of the core has a trans content of about 12% or less and a hardness of about 71 to 88 Shore C, the geometric center has a trans content of about 10% or less and a hardness of about 70

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to 80 Shore C, and the core surface hardness is greater than the geometric center hardness by about 1 to 10 Shore C to define a shallow positive hardness gradient.

In one embodiment, the positive hardness gradient is about 2 to 8 Shore C, more preferably about 2.5 to 7 Shore C. The core preferably has an outer diameter of about 1.45 to about 1.62 inches, more preferably about 1.50 to about 1.58 inches. The hardness of the geometric center of the core is generally about 72 to 78 Shore C and the hardness of the core surface is generally about 73 to 80 Shore C, more preferably about 74 to 78 Shore C. In another preferred embodiment, the outer surface of the core has a trans content of about 10% or less and the geometric center of the core has a trans content of about 8% or less.

The present invention is also directed to a golf ball formed from a single core having an outer diameter of about 1.5 to 1.55 inches. The core is typically formed from a substantially homogenous rubber composition. An inner cover layer is disposed about the core and is typically formed from a thermoplastic ionomeric material having a material hardness of about 66 to 80 Shore D. An outer cover layer is disposed about the inner cover layer and has a thickness of about 0.04 inches. In this embodiment, the outer cover layer is formed from an ionomer having a material hardness of about 64 to 68 Shore D, or a thermosetting castable polyurethane having a hardness of about 51 to 55 Shore D. Preferably, the outer surface of the core has a trans content of about 12% or less and a hardness of about 74 to 78 Shore C, the geometric center has a trans content of about 10% or less and a hardness of about 72 to 78 Shore C, and the core surface hardness is greater than the geometric center hardness by about 1 to 5 Shore C to define a shallow positive hardness gradient, the core having an Atti compression of about 50 to 70.

In one embodiment, the golf ball further includes an intermediate layer disposed between the inner cover layer and the core, the intermediate layer having a thickness of about 0.06 inches and a hardness of about 43 to 47 Shore D. Generally, the inner cover hardness is about 66 Shore D, the intermediate layer hardness is about 45 Shore D, and the outer cover layer hardness is about 53 Shore D.

The present invention is further directed to a golf ball including a single core having an outer diameter of about 1.45 inches, an outer surface, and a geometric center, and being formed from a substantially homogenous rubber composition. An inner cover layer is disposed about the core. The inner cover has an outer diameter of about 1.58 inches and is formed from a thermoplastic non-ionomeric material having a material hardness of about 38 to 42 Shore D. An outer cover layer is disposed about the inner cover layer. The outer cover has a thickness of about 0.05 inches and is formed from an ionomer having a material hardness of about 66 to 70 Shore D. Preferably, the outer surface of the core has a trans content of about 12% or less and a hardness of about 74 to 78 Shore C, the geometric center has a trans content of about 10% or less and a hardness of about 72 to 78 Shore C, and the core surface hardness is greater than the geometric center hardness by about 1 to 5 Shore C to define a shallow positive hardness gradient.

A golf ball comprising an inner core layer having an outer surface and a geometric center and being formed from a substantially homogenous rubber composition; an outer core layer disposed about the inner core layer to form a dual core; an inner cover layer disposed about the dual core, the inner cover comprising a high-acid ionomer and having a material hardness of about 66 to 75 Shore D, the high-acid ionomer having an acid content of about 16% or greater; and an outer cover layer disposed about the inner cover layer, the outer

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cover comprising a polyurethane and having a material hardness of about 38 Shore D to about 56 Shore D; wherein the inner core layer surface hardness is from 0 Shore C to 10 Shore C lower than the geometric center hardness to define a negative hardness gradient and the outer core layer has a surface hardness at least 10 Shore C greater than the geometric center hardness to define a dual core positive hardness gradient.

Preferably, the ionomer has an acid content of about 18.5% to about 21.5%. The dual core has an outer diameter of about 1.45 to about 1.62 inches, more preferably about 1.50 to about 1.58 inches. The hardness of the inner core layer geometric center is about 68 to 72 Shore C. The hardness of the inner core layer surface is about 68 to 72 Shore C. The dual core surface hardness is at least about 78 Shore C, more preferably at least about 85 Shore C. In one embodiment, the hardness of the outer surface of the dual core is about 15 Shore C or greater than the hardness at the geometric center. Alternatively, the hardness of the outer surface of the dual core is about 15 Shore C to about 20 Shore C greater than the hardness at the geometric center.

The present invention is further directed to a golf ball including an inner core layer having an outer surface and a geometric center and being formed from a substantially homogenous rubber composition, an outer core layer disposed about the inner core layer to form a dual core, an inner cover layer disposed about the dual core, the inner cover including a high-acid ionomer and having a material hardness of about 66 to 75 Shore D, the high-acid ionomer having an acid content of about 16% or greater, and an outer cover layer disposed about the inner cover layer. The outer cover includes a polyurethane and having a material hardness of about 38 Shore D to about 56 Shore D. The inner core surface hardness is preferably greater than the geometric center hardness by about 1 to 10 Shore C to define a shallow positive hardness gradient.

The positive hardness gradient is preferably about 1 to 5 Shore C. In another embodiment, the positive hardness gradient is about 2 to 8 Shore C, more preferably about 2.5 to 7 Shore C.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other aspects of the present invention may be more fully understood with reference to, but not limited by, the following drawings.

FIG. 1 is a representative cross section of a golf ball of the invention; and

FIG. 2 is a representative cross section of a 4-piece golf ball of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The golf balls of the present invention may include a single-layer (one-piece) golf ball, and multi-layer golf balls, such as one having a core and a cover surrounding the core, but are preferably formed from a core comprised of a solid center (otherwise known as an inner core) and an outer core layer, an inner cover layer and an outer cover layer. Of course, any of the core and/or the cover layers may include more than one layer. In a preferred embodiment, the core is formed of an inner core and an outer core layer where both the inner core and the outer core layer have a "soft-to-hard" hardness gradient (a "negative" hardness gradient) radially inward from each component's outer surface towards its innermost portion (i.e., the center of the inner core or the inner surface of the outer core layer), although alternative embodiments involv-

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ing varying direction and combination of hardness gradient amongst core components are also envisioned (e.g., a “negative” gradient in the center coupled with a “positive” gradient in the outer core layer, or vice versa).

The center of the core may also be a liquid-filled or hollow sphere surrounded by one or more intermediate and/or cover layers, or it may include a solid or liquid center around which tensioned elastomeric material is wound. Any layers disposed around these alternative centers may exhibit the inventive core hardness gradient (i.e., “negative”). The cover layer may be a single layer or, for example, formed of a plurality of layers, such as an inner cover layer and an outer cover layer.

As briefly discussed above, the inventive cores may have a hardness gradient defined by hardness measurements made at the surface of the inner core (or outer core layer) and radially inward towards the center of the inner core, typically at 2-mm increments. As used herein, the terms “negative” and “positive” refer to the result of subtracting the hardness value at the innermost portion of the component being measured (e.g., the center of a solid core or an inner core in a dual core construction; the inner surface of a core layer; etc.) from the hardness value at the outer surface of the component being measured (e.g., the outer surface of a solid core; the outer surface of an inner core in a dual core; the outer surface of an outer core layer in a dual core, etc.). For example, if the outer surface of a solid core has a lower hardness value than the center (i.e., the surface is softer than the center), the hardness gradient will be deemed a “negative” gradient (a smaller number—a larger number—a negative number). It is preferred that the inventive cores have a zero or a negative hardness gradient, more preferably between zero (0) and -10, most preferably between 0 and -5.

Preferably, the core layers (inner core or outer core layer) is made from a composition including at least one thermoset base rubber, such as a polybutadiene rubber, cured with at least one peroxide and at least one reactive co-agent, which can be a metal salt of an unsaturated carboxylic acid, such as acrylic acid or methacrylic acid, a non-metallic coagent, or mixtures thereof. Preferably, a suitable antioxidant is included in the composition. An optional soft and fast agent (and sometimes a cis-to-trans catalyst), such as an organosulfur or metal-containing organosulfur compound, can also be included in the core formulation.

Other ingredients that are known to those skilled in the art may be used, and are understood to include, but not be limited to, density-adjusting fillers, process aides, plasticizers, blowing or foaming agents, sulfur accelerators, and/or non-peroxide radical sources. The base thermoset rubber, 130 which can be blended with other rubbers and polymers, typically includes a natural or synthetic rubber. A preferred base rubber is 1,4-polybutadiene having a cis structure of at least 40%, preferably greater than 80%, and more preferably greater than 90%. Examples of desirable polybutadiene rubbers include BUNA® CB22 and BUNA® CB23, CB1221, CB1220, CB24, and CB21, commercially-available from LANXESS Corporation; UBEPOL® 360L and UBEPOL® 150L and UBEPOL-BR rubbers, commercially available from UBE Industries, Ltd. of Tokyo, Japan; KINEX® 7245, KINEX® 7265, and BUDENE 1207 and 1208, commercially available from Goodyear of Akron, Ohio; SE BR-1220; Europrene® NEOCIS® BR 40 and BR 60, commercially available from Polimeri Europa; and BR 01, BR 730, BR 735, BR 11, and BR 51, commercially available from Japan Synthetic Rubber Co., Ltd; PETROFLEX® BRNd-40; and KARBOCHEM® ND40, ND45, and ND60, commercially available from Karbochem.

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From the Lanxess Corporation, most preferred are the neodymium and cobalt catalyzed grades, but all of the following may be used: Buna CB 21; Buna CB 22; Buna CB 23; Buna CB 24; Buna CB 25; Buna CB 29 MES; Buna CB Nd 40; Buna CB Nd 40 H; Buna CB Nd 60; Buna CB 55 NF; Buna CB 60; Buna CB 45 B; Buna CB 55 B; Buna CB 55 H; Buna CB 55 L; Buna CB 70 B; Buna CB 1220; Buna CB 1221; Buna CB 1203; Buna CB 45. Additionally, numerous suitable rubbers are available from JSR (Japan Synthetic Rubber), Ube sold by Ube Industries Inc, Japan, BST sold by BST Elastomers, Thailand; IPCL sold by Indian Petrochemicals Ltd, India; Nitsu sold by Karbochem or Karbochem Ltd of South Africa; Petroflex of Brazil; LG of Korea; and Kuhmo Petrochemical of Korea.

The base rubber may also comprise high or medium Mooney viscosity rubber, or blends thereof. A “Mooney” unit is a unit used to measure the plasticity of raw or unvulcanized rubber. The plasticity in a “Mooney” unit is equal to the torque, measured on an arbitrary scale, on a disk in a vessel that contains rubber at a temperature of 100° C. and rotates at two revolutions per minute. The measurement of Mooney viscosity is defined according to ASTM D-1646. The Mooney viscosity range is preferably greater than about 40, more preferably in the range from about 40 to about 80 and more preferably in the range from about 40 to about 60. Polybutadiene rubber with higher Mooney viscosity may also be used, so long as the viscosity of the polybutadiene does not reach a level where the high viscosity polybutadiene clogs or otherwise adversely interferes with the manufacturing machinery. It is contemplated that polybutadiene with viscosity less than 65 Mooney can be used with the present invention. In one embodiment of the present invention, golf ball cores made with mid- to high-Mooney viscosity polybutadiene material exhibit increased resiliency (and, therefore, distance) without increasing the hardness of the ball. Such cores are soft, i.e., compression less than about 60 and more specifically in the range of about 50-55. Cores with compression in the range of from about 30 about 50 are also within the range of this preferred embodiment.

Commercial sources of suitable mid- to high-Mooney viscosity polybutadiene include Bayer AG CB23 (Nd-catalyzed), which has a Mooney viscosity of around 50 and is a highly linear polybutadiene, and CB1221 (Co-catalyzed). If desired, the polybutadiene can also be mixed with other elastomers known in the art, such as other polybutadiene rubbers, natural rubber, styrene butadiene rubber, and/or isoprene rubber in order to further modify the properties of the core. When a mixture of elastomers is used, the amounts of other constituents in the core composition are typically based on 100 parts by weight of the total elastomer mixture. In one preferred embodiment, the base rubber comprises a Nd-catalyzed polybutadiene, a rare earth-catalyzed polybutadiene rubber, or blends thereof. If desired, the polybutadiene can also be mixed with other elastomers known in the art such as natural rubber, polyisoprene rubber and/or styrene-butadiene rubber in order to modify the properties of the core. Other suitable base rubbers include thermosetting materials such as, ethylene propylene diene monomer rubber, ethylene propylene rubber, butyl rubber, halobutyl rubber, hydrogenated nitrile butadiene rubber, nitrile rubber, and silicone rubber.

Thermoplastic elastomers (TPE) may also be used to modify the properties of the core layers, or the uncured core layer stock by blending with the base thermoset rubber. These TPEs include natural or synthetic balata, or high trans-polyisoprene, high trans-polybutadiene, or any styrenic block copolymer, such as styrene ethylene butadiene styrene, styrene-isoprene-styrene, etc., a metallocene or other single-site

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catalyzed polyolefin such as ethylene-octene, or ethylene-butene, or thermoplastic polyurethanes (TPU), including copolymers, e.g. with silicone. Other suitable TPEs for blending with the thermoset rubbers of the present invention include PEBAX®, which is believed to comprise polyether amide copolymers, HYTREL®, which is believed to comprise polyether ester copolymers, thermoplastic urethane, and KRATON®, which is believed to comprise styrenic block copolymers elastomers. Any of the TPEs or TPUs above may also contain functionality suitable for grafting, including maleic acid or maleic anhydride.

Additional polymers may also optionally be incorporated into the base rubber. Examples include, but are not limited to, thermoset elastomers such as core regrind, thermoplastic vulcanizate, copolymeric ionomer, terpolymeric ionomer, polycarbonate, polyamide, copolymeric polyamide, polyesters, polyvinyl alcohols, acrylonitrile-butadiene-styrene copolymers, polyarylate, polyacrylate, polyphenylene ether, impact-modified polyphenylene ether, high impact polystyrene, diallyl phthalate polymer, styrene-acrylonitrile polymer (SAN) (including olefin-modified SAN and acrylonitrile-styrene-acrylonitrile polymer), styrene-maleic anhydride copolymer, styrenic copolymer, functionalized styrenic copolymer, functionalized styrenic terpolymer, styrenic terpolymer, cellulose polymer, liquid crystal polymer, ethylene-vinyl acetate copolymers, polyurea, and polysiloxane or any metallocene-catalyzed polymers of these species.

Suitable polyamides for use as an additional polymeric material in compositions within the scope of the present invention also include resins obtained by: (1) polycondensation of (a) a dicarboxylic acid, such as oxalic acid, adipic acid, sebacic acid, terephthalic acid, isophthalic acid, or 1,4-cyclohexanedicarboxylic acid, with (b) a diamine, such as ethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, or decamethylenediamine, 1,4-cyclohexanediamine, or m-xylylenediamine; (2) a ring-opening polymerization of cyclic lactam, such as ϵ -caprolactam or Ω -lauro lactam; (3) polycondensation of an aminocarboxylic acid, such as 6-aminocaproic acid, 9-aminononanoic acid, 11-aminoundecanoic acid, or 12-aminododecanoic acid; or (4) copolymerization of a cyclic lactam with a dicarboxylic acid and a diamine. Specific examples of suitable polyamides include NYLON 6, NYLON 66, NYLON 610, NYLON 11, NYLON 12, copolymerized NYLON, NYLON MXD6, and NYLON 46.

Suitable peroxide initiating agents include dicumyl peroxide; 2,5-dimethyl-2,5-di(t-butylperoxy) hexane; 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne; 2,5-dimethyl-2,5-di(benzoylperoxy)hexane; 2,2'-bis(t-butylperoxy)-di-isopropylbenzene; 1,1-bis(t-butylperoxy)-3,3,5-trimethyl cyclohexane; n-butyl 4,4-bis(t-butylperoxy)valerate; t-butyl perbenzoate; benzoyl peroxide; n-butyl 4,4'-bis(butylperoxy) valerate; di-t-butyl peroxide; or 2,5-di-(t-butylperoxy)-2,5-dimethyl hexane, lauryl peroxide, t-butyl hydroperoxide, α - α bis(t-butylperoxy)diisopropylbenzene, di(2-t-butylperoxyisopropyl)benzene, di-t-amyl peroxide, di-t-butyl peroxide. Preferably, the rubber composition includes from about 0.25 to about 5.0 parts by weight peroxide per 100 parts by weight rubber (phr), more preferably 0.5 phr to 3 phr, most preferably 0.5 phr to 1.5 phr. In a most preferred embodiment, the peroxide is present in an amount of about 0.8 phr. These ranges of peroxide are given assuming the peroxide is 100% active, without accounting for any carrier that might be present. Because many commercially available peroxides are sold along with a carrier compound, the actual amount of active peroxide present must be calculated. Commercially-available peroxide initiating agents include DICUP™ family of

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dicumyl peroxides (including DICUP™ R, DICUP™ 40C and DICUP™40KE) available from Crompton (Geo Specialty Chemicals). Similar initiating agents are available from AkroChem, Lanxess, Flexsys/Harwick and R.T. Vanderbilt. Another commercially-available and preferred initiating agent is TRIGONOX™ 265-50B from Akzo Nobel, which is a mixture of 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane and di(2-t-butylperoxyisopropyl)benzene. TRIGONOX™ peroxides are generally sold on a carrier compound.

Suitable reactive co-agents include, but are not limited to, metal salts of diacrylates, dimethacrylates, and monomethacrylates suitable for use in this invention include those wherein the metal is zinc, magnesium, calcium, barium, tin, aluminum, lithium, sodium, potassium, iron, zirconium, and bismuth. Zinc diacrylate (ZDA) is preferred, but the present invention is not limited thereto. ZDA provides golf balls with a high initial velocity. The ZDA can be of various grades of purity. For the purposes of this invention, the lower the quantity of zinc stearate present in the ZDA the higher the ZDA purity. ZDA containing less than about 10% zinc stearate is preferable. More preferable is ZDA containing about 4-8% zinc stearate. Suitable, commercially available zinc diacrylates include those from Sartomer Co. The preferred concentrations of ZDA that can be used are about 10 phr to about 40 phr, more preferably 20 phr to about 35 phr, most preferably 25 phr to about 35 phr. In a particularly preferred embodiment, the reactive co-agent is present in an amount of about 29 phr to about 31 phr.

Additional preferred co-agents that may be used alone or in combination with those mentioned above include, but are not limited to, trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, and the like. It is understood by those skilled in the art, that in the case where these co-agents may be liquids at room temperature, it may be advantageous to disperse these compounds on a suitable carrier to promote ease of incorporation in the rubber mixture.

Antioxidants are compounds that inhibit or prevent the oxidative breakdown of elastomers, and/or inhibit or prevent reactions that are promoted by oxygen radicals. Some exemplary antioxidants that may be used in the present invention include, but are not limited to, quinoline type antioxidants, amine type antioxidants, and phenolic type antioxidants. A preferred antioxidant is 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol) available as VANOX® MBPC from R.T. Vanderbilt. Other polyphenolic antioxidants include VANOX® T, VANOX® L, VANOX® SKT, VANOX® SWP, VANOX® 13 and VANOX® 1290.

Suitable antioxidants include, but are not limited to, alkylene-bis-alkyl substituted cresols, such as 4,4'-methylene-bis(2,5-xyleneol); 4,4'-ethylidene-bis-(6-ethyl-m-cresol); 4,4'-butylidene-bis-(6-tert-butyl-m-cresol); 4,4'-decylidene-bis-(6-methyl-m-cresol); 4,4'-methylene-bis-(2-amyl-m-cresol); 4,4'-propylidene-bis-(5-hexyl-m-cresol); 3,3'-decylidene-bis-(5-ethyl-p-cresol); 2,2'-butylidene-bis-(3-n-hexyl-p-cresol); 4,4'-(2-butylidene)-bis-(6-tert-butyl-m-cresol); 3,3'-4-(decylidene)-bis-(5-ethyl-p-cresol); (2,5-dimethyl-4-hydroxyphenyl) (2-hydroxy-3,5-dimethylphenyl) methane; (2-methyl-4-hydroxy-5-ethylphenyl) (2-ethyl-3-hydroxy-5-methylphenyl) methane; (3-methyl-5-hydroxy-6-tert-butylphenyl) (2-hydroxy-4-methyl-5-decylphenyl)-n-butyl methane; (2-hydroxy-4-ethyl-5-methylphenyl) (2-decyl-3-hydroxy-4-methylphenyl)butylamylmethane; (3-ethyl-4-methyl-5-hydroxyphenyl)-(2,3-dimethyl-3-hydroxy-phenyl)nonylmethane; (3-methyl-2-hydroxy-6-ethylphenyl)-(2-isopropyl-3-hydroxy-5-methyl-phenyl)cyclohexylmethane; (2-methyl-4-hydroxy-5-methylphenyl) (2-hydroxy-3-methyl-5-ethylphenyl)dicyclohexyl methane; and the like.

Other suitable antioxidants include, but are not limited to, substituted phenols, such as 2-tert-butyl-4-methoxyphenol; 3-tert-butyl-4-methoxyphenol; 3-tert-octyl-4-methoxyphenol; 2-methyl-4-methoxyphenol; 2-stearyl-4-n-butoxyphenol; 3-t-butyl-4-stearyl-4-methoxyphenol; 3-lauryl-4-methoxyphenol; 2,5-di-t-butyl-4-methoxyphenol; 2-methyl-4-methoxyphenol; 2-(1-methylcyclohexyl)-4-methoxyphenol; 2-t-butyl-4-dodecyloxyphenol; 2-(1-methylbenzyl)-4-methoxyphenol; 2-t-octyl-4-methoxyphenol; methyl gallate; n-propyl gallate; n-butyl gallate; lauryl gallate; myristyl gallate; stearyl gallate; 2,4,5-trihydroxyacetophenone; 2,4,5-trihydroxy-n-butylprophenone; 2,4,5-trihydroxystearophenone; 2,6-ditert-butyl-4-methylphenol; 2,6-ditert-octyl-4-methylphenol; 2,6-ditert-butyl-4-stearylphenol; 2-methyl-4-methyl-6-tert-butylphenol; 2,6-distearyl-4-methylphenol; 2,6-dilauryl-4-methylphenol; 2,6-di(n-octyl)-4-methylphenol; 2,6-di(n-hexadecyl)-4-methylphenol; 2,6-di(1-methylundecyl)-4-methylphenol; 2,6-di(1-methylheptadecyl)-4-methylphenol; 2,6-di(trimethylhexyl)-4-methylphenol; 2,6-di(1,1,3,3-tetramethyloctyl)-4-methylphenol; 2-n-dodecyl-6-tert-butyl-4-methylphenol; 2-n-dodecyl-6-(1-methylundecyl)-4-methylphenol; 2-n-dodecyl-6-(1,1,3,3-tetramethyloctyl)-4-methylphenol; 2-n-dodecyl-6-n-octadecyl-4-methylphenol; 2-n-dodecyl-6-n-octyl-4-methylphenol; 2-methyl-6-n-octadecyl-4-methylphenol; 2-n-dodecyl-6-(1-methylheptadecyl)-4-methylphenol; 2,6-di(1-methylbenzyl)-4-methylphenol; 2,6-di(1-methylcyclohexyl)-4-methylphenol; 2,6-(1-methylcyclohexyl)-4-methylphenol; 2-(1-methylbenzyl)-4-methylphenol; and related substituted phenols.

More suitable antioxidants include, but are not limited to, alkylene bisphenols, such as 4,4'-butylidene bis(3-methyl-6-t-butyl phenol); 2,2-butylidene bis(4,6-dimethyl phenol); 2,2'-butylidene bis(4-methyl-6-t-butyl phenol); 2,2'-butylidene bis(4-t-butyl-6-methyl phenol); 2,2'-ethylidene bis(4-methyl-6-t-butylphenol); 2,2'-methylene bis(4,6-dimethyl phenol); 2,2'-methylene bis(4-methyl-6-t-butyl phenol); 2,2'-methylene bis(4-ethyl-6-t-butyl phenol); 4,4'-methylene bis(2,6-di-t-butyl phenol); 4,4'-methylene bis(2-methyl-6-t-butyl phenol); 4,4'-methylene bis(2,6-dimethyl phenol); 2,2'-methylene bis(4-t-butyl-6-phenyl phenol); 2,2'-dihydroxy-3,3',5',5'-tetramethylstilbene; 2,2'-isopropylidene bis(4-methyl-6-t-butyl phenol); ethylene bis(beta-naphthol); 1,5-dihydroxy naphthalene; 2,2'-ethylene bis(4-methyl-6-propyl phenol); 4,4'-methylene bis(2-propyl-6-t-butyl phenol); 4,4'-ethylene bis(2-methyl-6-propyl phenol); 2,2'-methylene bis(5-methyl-6-t-butyl phenol); and 4,4'-butylidene bis(6-t-butyl-3-methyl phenol);

Suitable antioxidants further include, but are not limited to, alkylene trisphenols, such as 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methyl benzyl)-4-methyl phenol; 2,6-bis(2'-hydroxy-3'-t-ethyl-5'-butyl benzyl)-4-methyl phenol; and 2,6-bis(2'-hydroxy-3'-t-butyl-5'-propyl benzyl)-4-methyl phenol.

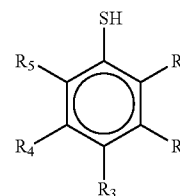
The antioxidant is typically present in an amount of about 0.1 phr to about 5 phr, preferably from about 0.1 phr to about 2 phr, more preferably about 0.1 phr to about 1 phr. In a particularly preferred embodiment, the antioxidant is present in an amount of about 0.4 phr. In an alternative embodiment, the antioxidant should be present in an amount to ensure that the hardness gradient of the inventive cores is negative. Preferably, about 0.2 phr to about 1 phr antioxidant is added to the core layer (inner core or outer core layer) formulation, more preferably, about 0.3 to about 0.8 phr, and most preferably 0.4 to about 0.7 phr. Preferably, about 0.25 phr to about 1.5 phr of peroxide as calculated at 100% active can be added to the core formulation, more preferably about 0.5 phr to about 1.2 phr, and most preferably about 0.7 phr to about 1.0 phr. The ZDA amount can be varied to suit the desired compression, spin

and feel of the resulting golf ball. The cure regime can have a temperature range between from about 290° F. to about 335° F., more preferably about 300° F. to about 325° F., and the stock is held at that temperature for at least about 10 minutes to about 30 minutes.

The thermoset rubber composition of the present invention may also include an optional soft and fast agent. As used herein, "soft and fast agent" means any compound or a blend thereof that that is capable of making a core 1) be softer (lower compression) at constant COR or 2) have a higher COR at equal compression, or any combination thereof, when compared to a core equivalently prepared without a soft and fast agent. Preferably, the composition of the present invention contains from about 0.05 phr to about 10.0 phr soft and fast agent. In one embodiment, the soft and fast agent is present in an amount of about 0.05 phr to about 3.0 phr, preferably about 0.05 phr to about 2.0 phr, more preferably about 0.05 phr to about 1.0 phr. In another embodiment, the soft and fast agent is present in an amount of about 2.0 phr to about 5.0 phr, preferably about 2.35 phr to about 4.0 phr, and more preferably about 2.35 phr to about 3.0 phr. In an alternative high concentration embodiment, the soft and fast agent is present in an amount of about 5.0 phr to about 10.0 phr, more preferably about 6.0 phr to about 9.0 phr, most preferably about 7.0 phr to about 8.0 phr. In a most preferred embodiment, the soft and fast agent is present in an amount of about 2.6 phr.

Suitable soft and fast agents include, but are not limited to, organosulfur or metal-containing organosulfur compounds, an organic sulfur compound, including mono, di, and polysulfides, a thiol, or mercapto compound, an inorganic sulfide compound, a Group VIA compound, or mixtures thereof. The soft and fast agent component may also be a blend of an organosulfur compound and an inorganic sulfide compound.

Suitable soft and fast agents of the present invention include, but are not limited to those having the following general formula:



where R₁-R₅ can be C₁-C₈ alkyl groups; halogen groups; thiol groups (—SH), carboxylated groups; sulfonated groups; and hydrogen; in any order; and also pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-io-

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dothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts. Preferably, the halogenated thiophenol compound is pentachlorothiophenol, which is commercially available in neat form or under the tradename STRUKTOL®, a clay-based carrier containing the sulfur compound pentachlorothiophenol loaded at 45 percent (correlating to 2.4 parts PCTP). STRUKTOL® is commercially available from Struktol Company of America of Stow, Ohio. PCTP is commercially available in neat form from eChinachem of San Francisco, Calif. and in the salt form from eChinachem of San Francisco, Calif. Most preferably, the halogenated thiophenol compound is the zinc salt of pentachlorothiophenol, which is commercially available from eChinachem of San Francisco, Calif.

As used herein when referring to the invention, the term “organosulfur compound(s)” refers to any compound containing carbon, hydrogen, and sulfur, where the sulfur is directly bonded to at least 1 carbon. As used herein, the term “sulfur compound” means a compound that is elemental sulfur, polymeric sulfur, or a combination thereof. It should be further understood that the term “elemental sulfur” refers to the ring structure of S₈ and that “polymeric sulfur” is a structure including at least one additional sulfur relative to elemental sulfur.

Additional suitable examples of soft and fast agents (that are also believed to be cis-to-trans catalysts) include, but are not limited to, 4,4'-diphenyl disulfide; 4,4'-ditolyl disulfide; 2,2'-benzamido diphenyl disulfide; bis(2-aminophenyl)disulfide; bis(4-aminophenyl)disulfide; bis(3-aminophenyl)disulfide; 2,2'-bis(4-aminonaphthyl)disulfide; 2,2'-bis(3-aminonaphthyl)disulfide; 2,2'-bis(4-aminonaphthyl)disulfide; 2,2'-bis(5-aminonaphthyl)disulfide; 2,2'-bis(6-aminonaphthyl)disulfide; 2,2'-bis(7-aminonaphthyl)disulfide; 2,2'-bis(8-aminonaphthyl)disulfide; 1,1'-bis(2-aminonaphthyl)disulfide; 1,1'-bis(3-aminonaphthyl)disulfide; 1,1'-bis(3-aminonaphthyl)disulfide; 1,1'-bis(4-aminonaphthyl)disulfide; 1,1'-bis(5-aminonaphthyl)disulfide; 1,1'-bis(6-aminonaphthyl)disulfide; 1,1'-bis(7-aminonaphthyl)disulfide; 1,1'-bis(8-aminonaphthyl)disulfide; 1,2'-diamino-1,2'-dithiodinaphthalene; 2,3'-diamino-1,2'-dithiodinaphthalene; bis(4-chlorophenyl)disulfide; bis(2-chlorophenyl)disulfide; bis(3-chlorophenyl)disulfide; bis(4-bromophenyl)disulfide; bis(2-bromophenyl)disulfide; bis(3-bromophenyl)disulfide; bis(4-fluorophenyl)disulfide; bis(4-iodophenyl)disulfide; bis(2,5-dichlorophenyl)disulfide; bis(3,5-dichlorophenyl)disulfide; bis(2,4-dichlorophenyl)disulfide; bis(2,6-dichlorophenyl)disulfide; bis(2,5-dibromophenyl)disulfide; bis(3,5-dibromophenyl)disulfide; bis(2-chloro-5-bromophenyl)disulfide; bis(2,4,6-trichlorophenyl)disulfide; bis(2,3,4,5,6-pentachlorophenyl)disulfide; bis(4-cyanophenyl)disulfide; bis(2-cyanophenyl)disulfide; bis(4-nitrophenyl)disulfide; bis(2-nitrophenyl)disulfide; 2,2'-dithiobenzoic acid ethylester; 2,2'-dithiobenzoic acid methylester; 2,2'-dithiobenzoic acid; 4,4'-dithiobenzoic acid ethylester; bis(4-acetylphenyl)disulfide; bis(2-acetylphenyl)disulfide; bis(4-formylphenyl)disulfide; bis(4-carbamoylphenyl)disulfide; 1,1'-dinaphthyl disulfide; 2,2'-dinaphthyl disulfide; 1,2'-dinaphthyl disulfide; 2,2'-bis(1-chlorodinaphthyl)disulfide; 2,2'-bis(1-bromonaphthyl)disulfide; 1,1'-bis(2-chloronaphthyl)disulfide; 2,2'-bis(1-cyanonaphthyl)disulfide; 2,2'-bis(1-acetylnaphthyl)disulfide; and the like; or a mixture thereof. Preferred organosulfur components include 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide, or a mixture thereof. A more preferred organosulfur component includes

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4,4'-ditolyl disulfide. In another embodiment, metal-containing organosulfur components can be used according to the invention. Suitable metal-containing organosulfur components include, but are not limited to, cadmium, copper, lead, and tellurium analogs of diethyldithiocarbamate, diamyldithiocarbamate, and dimethyldithiocarbamate, or mixtures thereof.

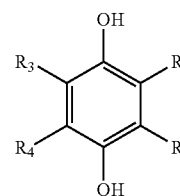
Suitable substituted or unsubstituted aromatic organic components that do not include sulfur or a metal include, but are not limited to, 4,4'-diphenyl acetylene, azobenzene, or a mixture thereof. The aromatic organic group preferably ranges in size from C₆ to C₂₀, and more preferably from C₆ to C₁₀. Suitable inorganic sulfide components include, but are not limited to titanium sulfide, manganese sulfide, and sulfide analogs of iron, calcium, cobalt, molybdenum, tungsten, copper, selenium, yttrium, zinc, tin, and bismuth.

A substituted or unsubstituted aromatic organic compound is also suitable as a soft and fast agent. Suitable substituted or unsubstituted aromatic organic components include, but are not limited to, components having the formula (R₁)_x—R₃—M—R₄—(R₂)_y, wherein R₁ and R₂ are each hydrogen or a substituted or unsubstituted C₁₋₂₀ linear, branched, or cyclic alkyl, alkoxy, or alkylthio group, or a single, multiple, or fused ring C₆ to C₂₄ aromatic group; x and y are each an integer from 0 to 5; R₃ and R₄ are each selected from a single, multiple, or fused ring C₆ to C₂₄ aromatic group; and M includes an azo group or a metal component. R₃ and R₄ are each preferably selected from a C₆ to C₁₀ aromatic group, more preferably selected from phenyl, benzyl, naphthyl, benzamido, and benzothiazyl. R₁ and R₂ are each preferably selected from a substituted or unsubstituted C₁₋₁₀ linear, branched, or cyclic alkyl, alkoxy, or alkylthio group or a C₆ to C₁₀ aromatic group. When R₁, R₂, R₃, or R₄ are substituted, the substitution may include one or more of the following substituent groups: hydroxy and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carbonyl including esters, acids, and metal salts thereof; silyl; acrylates and metal salts thereof; sulfonyl or sulfonamide; and phosphates and phosphites. When M is a metal component, it may be any suitable elemental metal available to those of ordinary skill in the art. Typically, the metal will be a transition metal, although preferably it is tellurium or selenium. In one embodiment, the aromatic organic compound is substantially free of metal, while in another embodiment the aromatic organic compound is completely free of metal.

The soft and fast agent can also include a Group VIA component. Elemental sulfur and polymeric sulfur are commercially available from Elastochem, Inc. of Chardon, Ohio. Exemplary sulfur catalyst compounds include PB(RM-S)-80 elemental sulfur and PB(CRST)-65 polymeric sulfur, each of which is available from Elastochem, Inc. An exemplary tellurium catalyst under the tradename TELLOY® and an exemplary selenium catalyst under the tradename VANDEX® are each commercially available from RT Vanderbilt.

Other suitable soft and fast agents include, but are not limited to, hydroquinones, benzoquinones, quinhydrone, catechols, and resorcinols.

Suitable hydroquinone compounds include compounds represented by the following formula, and hydrates thereof:



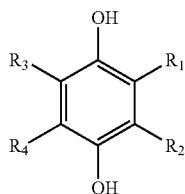
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wherein each R_1 , R_2 , R_3 , and R_4 are hydrogen; halogen; alkyl; carboxyl; metal salts thereof; and esters thereof; acetate and esters thereof; formyl; acyl; acetyl; halogenated carbonyl; sulfo and esters thereof; halogenated sulfonyl; sulfinio; alkyl-sulfinyl; carbamoyl; halogenated alkyl; cyano; alkoxy; hydroxy and metal salts thereof; amino; nitro; aryl; aryloxy; arylalkyl; nitroso; acetamido; or vinyl.

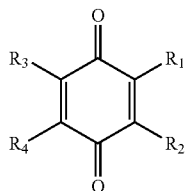
Other suitable hydroquinone compounds include, but are not limited to, hydroquinone; tetrachlorohydroquinone; 2-chlorohydroquinone; 2-bromohydroquinone; 2,5-dichlorohydroquinone; 2,5-dibromohydroquinone; tetrabromohydroquinone; 2-methylhydroquinone; 2-t-butylhydroquinone; 2,5-di-t-amylhydroquinone; and 2-(2-chlorophenyl) hydroquinone hydrate.

More suitable hydroquinone compounds include compounds represented by the following formula, and hydrates thereof:



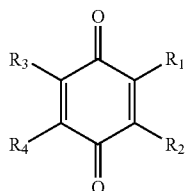
wherein each R_1 , R_2 , R_3 , and R_4 are a metal salt of a carboxyl; acetate and esters thereof; hydroxy; a metal salt of a hydroxy; amino; nitro; aryl; aryloxy; arylalkyl; nitroso; acetamido; or vinyl.

Suitable benzoquinone compounds include compounds represented by the following formula, and hydrates thereof:



wherein each R_1 , R_2 , R_3 , and R_4 are hydrogen; halogen; alkyl; carboxyl; metal salts thereof; and esters thereof; acetate and esters thereof; formyl; acyl; acetyl; halogenated carbonyl; sulfo and esters thereof; halogenated sulfonyl; sulfinio; alkyl-sulfinyl; carbamoyl; halogenated alkyl; cyano; alkoxy; hydroxy and metal salts thereof; amino; nitro; aryl; aryloxy; arylalkyl; nitroso; acetamido; or vinyl.

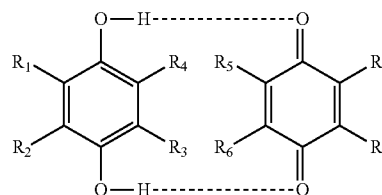
Other suitable benzoquinone compounds include one or more compounds represented by the following formula, and hydrates thereof:



wherein each R_1 , R_2 , R_3 , and R_4 are a metal salt of a carboxyl; acetate and esters thereof; hydroxy; a metal salt of a hydroxy; amino; nitro; aryl; aryloxy; arylalkyl; nitroso; acetamido; or vinyl.

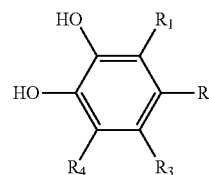
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Suitable quinhydrones include one or more compounds represented by the following formula, and hydrates thereof:



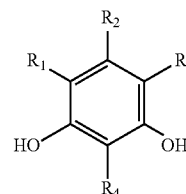
wherein each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 are hydrogen; halogen; alkyl; carboxyl; metal salts thereof; and esters thereof; acetate and esters thereof; formyl; acyl; acetyl; halogenated carbonyl; sulfo and esters thereof; halogenated sulfonyl; sulfinio; alkylsulfinyl; carbamoyl; halogenated alkyl; cyano; alkoxy; hydroxy and metal salts thereof; amino; nitro; aryl; aryloxy; arylalkyl; nitroso; acetamido; or vinyl.

Other suitable quinhydrones include those having the above formula, wherein each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 are a metal salt of a carboxyl; acetate and esters thereof; hydroxy; a metal salt of a hydroxy; amino; nitro; aryl; aryloxy; arylalkyl; nitroso; acetamido; or vinyl. Suitable catechols include one or more compounds represented by the following formula, and hydrates thereof:



wherein each R_1 , R_2 , R_3 , and R_4 are hydrogen; halogen; alkyl; carboxyl; metal salts thereof; and esters thereof; acetate and esters thereof; formyl; acyl; acetyl; halogenated carbonyl; sulfo and esters thereof; halogenated sulfonyl; sulfinio; alkyl-sulfinyl; carbamoyl; halogenated alkyl; cyano; alkoxy; hydroxy and metal salts thereof; amino; nitro; aryl; aryloxy; arylalkyl; nitroso; acetamido; or vinyl.

Suitable resorcinols include one or more compounds represented by the following formula, and hydrates thereof:



wherein each R_1 , R_2 , R_3 , and R_4 are hydrogen; halogen; alkyl; carboxyl; metal salts thereof; and esters thereof; acetate and esters thereof; formyl; acyl; acetyl; halogenated carbonyl; sulfo and esters thereof; halogenated sulfonyl; sulfinio; alkyl-sulfinyl; carbamoyl; halogenated alkyl; cyano; alkoxy; hydroxy and metal salts thereof; amino; nitro; aryl; aryloxy; arylalkyl; nitroso; acetamido; or vinyl.

Fillers may also be added to the thermoset rubber composition of the core to adjust the density of the composition, up or down. Typically, fillers include materials such as tungsten,

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zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate, metals, metal oxides and salts, regrind (recycled core material typically ground to about 30 mesh particle), high-Mooney-viscosity rubber regrind, trans-regrind core material (recycled core material containing high trans-isomer of polybutadiene), and the like. When trans-regrind is present, the amount of trans-isomer is preferably between about 10% and about 60%. In a preferred embodiment of the invention, the core comprises polybutadiene having a cis-isomer content of greater than about 95% and trans-regrind core material (already vulcanized) as a filler. Any particle size trans-regrind core material is sufficient, but is preferably less than about 125 μm .

Fillers added to one or more portions of the golf ball typically include processing aids or compounds to affect rheological and mixing properties, density-modifying fillers, tear strength, or reinforcement fillers, and the like. The fillers are generally inorganic, and suitable fillers include numerous metals or metal oxides, such as zinc oxide and tin oxide, as well as barium sulfate, zinc sulfate, calcium carbonate, barium carbonate, clay, tungsten, tungsten carbide, an array of silicas, and mixtures thereof. Fillers may also include various foaming agents or blowing agents which may be readily selected by one of ordinary skill in the art. Fillers may include polymeric, ceramic, metal, and glass microspheres may be solid or hollow, and filled or unfilled. Fillers are typically also added to one or more portions of the golf ball to modify the density thereof to conform to uniform golf ball standards. Fillers may also be used to modify the weight of the center or at least one additional layer for specialty balls, e.g., a lower weight ball is preferred for a player having a low swing speed.

Materials such as tungsten, zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate, metals, metal oxides and salts, and regrind (recycled core material typically ground to about 30 mesh particle) are also suitable fillers.

The polybutadiene and/or any other base rubber or elastomer system may also be foamed, or filled with hollow microspheres or with expandable microspheres which expand at a set temperature during the curing process to any low specific gravity level. Other ingredients such as sulfur accelerators, e.g., tetramethylthiuram di, tri, or tetrasulfide, and/or metal-containing organosulfur components may also be used according to the invention. Suitable metal-containing organosulfur accelerators include, but are not limited to, cadmium, copper, lead, and tellurium analogs of diethyldithiocarbamate, diamyldithiocarbamate, and dimethyldithiocarbamate, or mixtures thereof. Other ingredients such as processing aids e.g., fatty acids and/or their metal salts, processing oils, dyes and pigments, as well as other additives known to one skilled in the art may also be used in the present invention in amounts sufficient to achieve the purpose for which they are typically used.

Without being bound by theory, it is believed that the percentage of double bonds in the trans configuration may be manipulated throughout a core containing at least one main-chain unsaturated rubber (i.e., polybutadiene), plastic, or elastomer resulting in a trans gradient. The trans gradient may be influenced (up or down) by changing the type and amount of cis-to-trans catalyst (or soft-and-fast agent), the type and amount of peroxide, and the type and amount of coagent in the formulation. For example, a formulation containing about 0.25 phr ZnPCTP may have a trans gradient of about 5% across the core whereas a formulation containing about 2 phr ZnPCTP may have a trans gradient of about 10%, or higher. The trans gradient may also be manipulated through the cure times and temperatures. It is believed that lower temperatures

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and shorter cure times yield lower trans gradients, although a combination of many of these factors may yield gradients of differing and/or opposite directions from that resulting from use of a single factor.

The % trans isomer in a core can also be manipulated by adding organosulfur compounds, such as those listed above, to the core formulation including but not limited to pentachlorothiophenol, zinc pentachlorothiophenol, ditolyl disulfide, and diphenyl disulfide. The amount of the organosulfur compound and the overall state of cure affect the amount of the trans isomer that is produced during the cure reaction. Another method of increasing the trans content in a core is to introduce an unsaturated rubber that contains a high level of trans isomer, such as high trans containing polybutadiene or high trans containing polyoctenamer into the core formulation. High trans rubber can be used with or without the organosulfur compounds.

In general, higher and/or faster cure rates tend to yield higher levels of trans content, as do higher concentrations of peroxides, soft-and-fast agents, and, to some extent, ZDA concentration. Even the type of rubber may have an effect on trans levels, with those catalyzed by rare-earth metals, such as Nd, being able to form higher levels of trans polybutadiene compared to those rubbers formed from Group VIII metals, such as Co, Ni, and Li.

The measurement of trans-isomer content of polybutadiene referred to herein was and can be accomplished as follows. Calibration standards are prepared using at least two polybutadiene rubber samples of known trans content, e.g., high and low percent trans-polybutadiene. These samples are used alone and blended together in such a way as to create a ladder of trans-polybutadiene content of at least about 1.5% to 50% or to bracket the unknown amount, such that the resulting calibration curve contains at least about 13 equally-spaced points.

Using a commercially-available FTIR spectrometer equipped with a Photoacoustic ("PAS") cell, a PAS spectrum of each standard was obtained using the following instrument parameters: scan at speed of 2.5 KHz (0.16 cm/s optical velocity), use a 1.2 KHz electronic filter, set an undersampling ratio of 2 (number of laser signal zero crossings before collecting a sample), co-add a minimum of 128 scans at a resolution of 4 cm^{-1} over a range of 375 to 4000 cm^{-1} with a sensitivity setting of 1.

The cis-, trans-, and vinyl-polybutadiene peaks are found between 600-1100 cm^{-1} in the PAS spectrum. The area under each of the trans-polybutadiene peaks can be integrated. Determining the fraction of each peak area relative to the total area of the three isomer peaks allow construction of a calibration curve of the trans-polybutadiene area fraction versus the actual trans-polybutadiene content. The correlation coefficient (R^2) of the resulting calibration curve must be a minimum of 0.95.

A PAS spectrum is obtained, using the parameters described above, for the unknown core material at the point of interest (e.g., the surface or center of the core) by filling the PAS cell with a sample containing a freshly cut, uncontaminated surface free of foreign matters, such as mold release and the like. The trans-polybutadiene area fraction of the unknown is analyzed to determine the actual trans-isomer content from the calibration curve.

In one known circumstance when barium sulfate is included, the above method for testing trans-content may be less accurate. Thus, an additional or alternative test of the trans-content of polybutadiene is as follows. Calibration standards are prepared using at least two polybutadienes of known trans-content (e.g., high and low percent trans-polyb-

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utadiene). These samples are used alone and blended together in such a way as to create a ladder of trans-polybutadiene content of at least about 1.5% to 50% or to bracket the unknown amount, such that the resulting calibration curve contains at least about 13 equally-spaced points.

Using an FT-Raman spectrometer equipped with a near-infrared laser, a Stokes Raman spectrum should be obtained from each standard using the following instrument parameters: sufficient laser power (typically 400-800 mW) to obtain good signal-to-noise ratio without causing excessive heating or fluorescence; a resolution of 2 cm^{-1} ; over a Raman shift spectral range of $400\text{-}4000\text{ cm}^{-1}$; and co-adding at least 300 scans.

A calibration curve may be constructed from the data generated above, using a chemometrics approach and software, such as PLSplus/IQ from Galactic Industries Corp. An acceptable calibration was obtained with this software using a PLS-1 curve generated using an SNV (detrend) pathlength correction, a mean center data preparation, and a 5-point SG second derivative over the spectral range of $1600\text{-}1700\text{ cm}^{-1}$. The correlation coefficient (R^2) of the resulting calibration curve must be at least 0.95.

Preferably, the geometric center of the core has a trans content of about 1% to 10%, more preferably 2% to 9%, and most preferably 4% to 8%. The outer surface of the core preferably has a trans content of about 5% to 15%, more preferably about 7% to 12%, and most preferably about 8% to 10%. A half-radius point in the core preferably has a trans content of about 5% to 16%, more preferably about 6% to 14%, and most preferably about 7% to 13%.

Cores most suitable for the golf balls of the present invention have an outer surface and a center and are formed from a substantially homogenous rubber composition. An intermediate layer, such as a casing layer (inner cover), is disposed about the core, and a cover layer is formed around the intermediate layer, the cover typically formed from a castable polyurea or a castable polyurethane (i.e., meaning covers comprising castable polyurea (100% urea linkages/no urethane linkages); castable polyurethane (100% urethane linkages/no urea linkages); castable hybrid poly(urethane/urea) (the prepolymer is all urethane linkages and is cured with an amine); and castable hybrid poly(urea/urethane) (the prepolymer is all urea linkages and is cured with a polyol). In a preferred embodiment, the outer surface of the core has a trans-polybutadiene content of about 6% to 10%, the center of the core has a trans-polybutadiene content of about 1% to 3%, and the trans content of the outer surface of the core is greater than the trans content of the center by about 6% or greater to define a positive trans gradient along the core radius (i.e., the surface trans content is higher than the center trans content—a core having the opposite disposition of trans content would be considered to have a negative trans gradient and is also envisioned herein).

Referring to FIG. 1, in one embodiment of the present invention the golf ball 10 includes a core 12, an inner cover layer 14, and an outer cover layer 16. Referring to FIG. 2, in an alternative embodiment of the present invention the golf ball 10 includes an inner core layer 12, an inner cover layer 14, and an outer core layer 16 disposed between inner core layer 12 and inner cover layer 14. An outer cover layer 18 is disposed about inner cover layer 14.

The invention preferably includes a core of at least a single layer, the core having a “low hardness gradient” formulation and cure cycle, herein defined as a “LOG” core. Such LOG cores may have a “positive” Shore C hardness gradient (defined as the core surface hardness minus the geometric center hardness) of from about 1 Shore C to about 10 Shore C, more

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preferably about 2 Shore C to less than 8 Shore C, and most preferably about 2.5 Shore C to 7.5 Shore C. Where the LOG core includes more than one layer, e.g., a center surrounded by an outer core layer, either or both of the layers may have a low (or shallow) “positive” hardness gradient.

In a preferred embodiment of the present invention, the golf ball has a dual core, where the center (“inner core layer”) has a low hardness gradient across the cross section. Preferably the LOG center is a negative hardness gradient or, alternatively, a positive hardness gradient. As discussed herein, the overall dual core hardness gradient is preferably a positive hardness gradient, more preferably about 10 to 20, most preferably about 15 to 20.

The balls of the present invention preferably include at least a LOG core, a cover layer. Optionally, one or more intermediate layer(s) between the core and cover layer is present. Most preferably, a single layer LOG core having a diameter of about 1.45 to 1.62 inches, more preferably about 1.50 to 1.58 inches, and most preferably about 1.51 to 1.55 inches, is enclosed with two cover layers. The inner cover layer is preferably formed from an ionomeric material, such as a conventional ionomer or a highly-/fully-neutralized ionomer, having a hardness of about 60 Shore D or greater. The outer cover layer is preferably formed from polyurethane, polyurea, or a blend thereof, or a copolymer or hybrid thereof, having a hardness about 60 Shore D or less. In this most preferred embodiment, the LOG core has a geometric center hardness of about 70 to 80 Shore C, more preferably about 72 to 78 Shore C, and a surface hardness of about 71 to 88 Shore C, more preferably about 73 to 80 Shore C, and most preferably, about 74 to 78 Shore C. The LOG core also preferably has a compression (Atti) of about 50 to 90, more preferably about 60 to 80, and a surface trans-polybutadiene content of about 10% or less and a trans-polybutadiene content at the geometric center of about 8% or less.

The optional intermediate layer may be either relatively-hard (Shore C hardness of at least about 85, preferably at least about 90; and a Shore D hardness of at least about 61, preferably at least about 63) or relatively-soft (Shore C hardness about 85 or less, preferably about 83 or less, and a Shore D hardness of about 61 or less, preferably about 57 or less). The intermediate layer may include either a thermoplastic or thermosetting polymeric compositions. Thermosetting compositions include diene rubber based compositions, such as a peroxide or sulfur cured PBR, SBR, EPDM, NR, etc., or a polyurethane, polyurea, epoxy, urethane-acrylate, etc. Thermoplastic materials include ionomers, non-ionomers, polyesters, polyamides, PEBAX or HYTREL TPE's, and styrene-block copolymers (SBS, SEBS, etc).

Cover materials may be any of the same materials disclosed as suitable intermediate layer materials, and may even include a LOG or zero- or low-hardness-gradient rubber formulation/cure, but preferably include an ionomer, a polyurethane, or a polyurea. The cover layer(s) may be either hard or soft, with hardness values as described for the intermediate layers above.

The single (preferably), multi-layer, or multi-piece core may have a diameter of about 0.80 to 1.62 inches, preferably about 1.1 to 1.62 inches, more preferably about 1.2 to 1.60 inches, and most preferably about 1.3 to 1.58 inches. The combination of the LOG core and the intermediate layer(s) preferably have an outer diameter of about 1.0 to 1.66 inches, more preferably about 1.25 to 1.64 inches, and most preferably about 1.40 to 1.62 inches. The cover layer preferably had a thickness of about 0.010 to 0.080 inches, more preferably about 0.015 to 0.060 inches, and most preferably about 0.020 to 0.040 inches.

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Generally when a harder cover is employed, it is typically coupled with a relatively-soft intermediate layer to produce a relatively low-spinning golf ball. When a softer cover is used, it is typically coupled with a relatively hard intermediate layer to produce a golf ball having higher spin rates than the same construction using a hard cover. In alternative embodiments, a hard cover can be used with a hard intermediate layer or a soft cover can be used with a soft intermediate layer. It should be understood that the term 'hard' refers to a Shore D hardness of 55 or greater, the term 'soft' refers to a Shore D hardness of 45 or less; a 'typical' hardness would be 45 to 55 Shore D.

In another preferred embodiment the golf ball includes three layers. A LOG core preferably has a shallow "positive" hardness gradient of about 1 to 5 Shore C, a diameter of about 1.55 inches, a compression of about 50 to 100, preferably 65 to 85, and a COR of about 0.800-0.815, preferably 0.800-0.810. The intermediate layer is formed from a thermoplastic ionomer-based composition having a hardness of about 80 Shore C and an outer diameter of about 1.60 inches. A single cover layer is formed from an ionomer and has a thickness of about 0.040 inches and a hardness of about 66 Shore D. An alternative low-compression center embodiment may include a center having a compression of about 1 to 50, more preferably about 10 to 40, most preferably about 15 to 35.

The core of the present invention may also have a Soft Center Deflection Index ("SCDI") compression of less than about 160, more preferably, from about 40 and about 160, and most preferably, from about 60 and about 120.

The SCDI is a program change for the Dynamic Compression Machine ("DCM") that allows determination of the pounds required to deflect a core 10% of its diameter. The DCM is an apparatus that applies a load to a core or ball and measures the number of inches the core or ball is deflected at measured loads. A crude load/deflection curve is generated that is fit to the Atti compression scale that results in a number being generated that represents an Atti compression. The DCM does this via a load cell attached to the bottom of a hydraulic cylinder that is triggered pneumatically at a fixed rate (typically about 1.0 ft/s) towards a stationary core. Attached to the cylinder is an LVDT that measures the distance the cylinder travels during the testing timeframe. A software-based logarithmic algorithm ensures that measurements are not taken until at least five successive increases in load are detected during the initial phase of the test.

The SCDI is a slight variation of this set up. The hardware is the same, but the software and output has changed. With the SCDI, the interest is in the pounds of force required to deflect a core x amount of inches. That amount of deflection is 10% percent of the core diameter. The DCM is triggered, the cylinder deflects the core by 10% of its diameter, and the DCM reports back the pounds of force required (as measured from the attached load cell) to deflect the core by that amount. The value displayed is a single number in units of pounds.

Alternatively, the LOG core of the previous embodiment has a diameter of about 1.450 inches and is encased with an intermediate layer formed from a non-ionomeric thermoplastic (i.e., a PEBAX-type ester-amide block copolymer) having a of about 40 Shore D and an outer diameter of about 1.580 inches. A preferred cover layer is an ionomeric cover layer having a hardness of about 68 Shore D and a thickness of about 0.050 inches.

In still another preferred embodiment, the golf ball includes four layers. The core is formed from a LOG formula as described above and has an outer diameter of about 1.50 inches. The golf ball includes two intermediate layers, each having a thickness of about 0.060 inches. The innermost

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intermediate layer preferably has a hardness of about 45 Shore D and the outermost intermediate layer has a hardness of about 66 Shore D. The cover layer has a thickness of about 0.030 inches and is formed from a thermosetting, castable polyurethane or polyurea and has a hardness of about 53 Shore D.

In a fourth preferred embodiment, the golf ball includes four layers. The core includes a LOG center having a diameter of about 1.0 inch and an outer core layer. The outer core layer has an outer diameter of about 1.540 inches and a surface hardness of about 89 to 92 Shore C. The outer core layer is formed from a "conventional" polybutadiene rubber formulation and not a LOG formula. The intermediate layer is formed from an ionomer-based material and has an outer diameter of about 1.62 inches and a hardness of about 67 Shore D. The cover is formed from a cast polyurethane or polyurea and has a hardness of about 45 Shore D.

The hardness of the outer surface of the core may be lower than a hardness of the geometric center to define a negative hardness gradient of about -1 to about -15, more preferably about -5 to -10. The outer surface of the core may have a hardness of about 68 to about 80 Shore C and the geometric center has a hardness of about 68 to 80 Shore C. A hardness measured at the outer surface of the core may also be greater than a hardness of the core center to define a positive hardness gradient of about 0 to 5, more preferably about 2 to 5. The core preferably has a diameter of about 1.5 inches to 1.59 inches, more preferably about 1.51 to 1.57 inches, most preferably about 1.51 inches to 1.55 inches, including, specifically, 1.51 inches, 1.53 inches, or 1.55 inches.

The above embodiments may be tailored to meet predetermined performance properties. For example, alternative embodiments include those having an inner core having an outer diameter of about 0.250 inches to about 1.550 inches, preferably about 0.500 inches to about 1.500 inches, and more preferably about 0.750 inches to about 1.400 inches. In preferred embodiments, the inner core has an outer diameter of about 1.000 inch, 1.200 inches, or 1.300 inches, with a most preferred outer diameter being 1.130 inches. The outer core layer should have an outer diameter (the entire dual core) of about 1.30 inches to about 1.620 inches, preferably 1.400 inches to about 1.600 inches, and more preferably about 1.500 inches to about 1.590 inches. In preferred embodiments, the outer core layer has an outer diameter of about 1.510 inches, 1.530 inches, or most preferably 1.550 inches.

A number of cores were formed based on the formulation and cure cycle described in TABLE 1 below and core hardness values are reported in TABLE 2 below.

TABLE 1

Formulation (phr)				Comp		
	Ex 1	Ex 2	Ex 3	Ex 1	Ex 2	Ex 3
SR-526*	34.0	34.0	31.2	29.0	29.0	29.0
ZnO	5	5	5	5	5	5
BaSO ₄	11.2	11.2	16.1	13.8	13.8	13.8
VANOX	0.40	0.40	0.40	—	0.50	—
MBPC*	—	—	—	—	—	—
TRIGONOX-265-50B**	1.4	1.4	1.6	—	—	0.8
PERKADOX	—	—	—	1.0	1.6	—
BC-FF***	—	—	—	—	—	—
polybutadiene	100	100	100	100	100	100
ZnPCTP	2.35	2.35	2.60	2.35	2.35	2.35
regrind	—	—	17	17	—	—
antioxidant/ initiator ratio	0.57	0.57	0.50	—	0.31	—

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TABLE 1-continued

Formulation (phr)	Ex 1	Ex 2	Ex 3	Comp Ex 1	Comp Ex 2	Comp Ex 3
Cure Temp. (° F.)	305	315	320	350	335	335
Cure Time (min)	14	11	16	11	11	11
Properties						
diameter (in)	1.530	1.530	1.530	1.530	1.530	1.530
Atti compression	69	63	70	69	47	—
COR @ 125 ft/s	0.808	0.806	0.804	0.804	—	—

*VANOX ® MBPC: 2,2'-methylene-bis-(4-methyl-6-t-butylphenol) available from R. T. Vanderbilt Company Inc.;
 **TRIGONOX ® 265-50B: a mixture of 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane and di(2-t-butylperoxyisopropyl)benzene 50% active on an inert carrier available from Akzo Nobel;
 ***PERKADOX ® BC-FF: Dicumyl peroxide (99%-100% active) available from Akzo Nobel; and
 †SR-526: ZDA available from Sartomer

TABLE 2

Distance from Center	Shore C Hardness					
	Ex 1	Ex 2	Ex 3	Comp Ex 1	Comp Ex 2	Comp Ex 3
Center	73	70	71	61	52	61
2	74	71	72	67	57	62
4	74	72	73	70	62	65
6	75	73	73	72	64	67
8	75	73	73	73	64	69
10	75	73	74	73	64	71
12	74	74	73	72	66	72
14	74	74	72	73	70	73
16	70	71	70	77	71	73
18	60	60	63	80	72	73
Surface	63	70	66	85	73	74
Surface - Center	-10	0	-5	24	21	13

A number of cores were prepared and hardness measurements were made across the core. The cores, designated as Examples 1-4 in Table 3 below, all had an outer diameter of 1.53 inches. The hardness, in Shore C, was measured according to ASTM D-2240 at various locations across a cross-section of the core. The hardness results are tabulated below for the geometric center, outer surface, and at locations 2-mm, 4-mm, 6-mm, 8-mm, 10-mm, 12-mm, 14-mm, 16-mm, and 18-mm radially-outward from the geometric center of the core. The general core formulation included at least 85 phr CB1221 polybutadiene rubber, at least 15 phr CB23 polybutadiene rubber, about 35 phr zinc diacrylate, about 1 phr peroxide, about 0.5 phr VANOX® MBPC, about 5 phr ZnO, about 0.5 phr ZnPCTP, about 1 phr AFLUX® 16, about 13 phr POLYWATE® 325, and about 15 phr regrind. The cure cycles were adjusted, as necessary, to vary the hardness gradient across the core. Temperature/time criteria varied between about 330° F./20 min, 335° F./18 min, 340° F./16 min, and 345° F./14 min.

TABLE 3

Core Location	Ex A hardness (Shore C)	Ex B hardness (Shore C)	Ex C hardness (Shore C)	Ex D hardness (Shore C)
Center	73.1	73.1	72.1	73.9
2 mm	72.2	72.1	73.2	75.2
4 mm	72.9	73.9	75.3	75.9
6 mm	73.7	74.3	76.5	77.2

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TABLE 3-continued

Core Location	Ex A hardness (Shore C)	Ex B hardness (Shore C)	Ex C hardness (Shore C)	Ex D hardness (Shore C)
8 mm	74.0	74.3	76.5	77.1
10 mm	74.7	73.8	76.5	76.7
12 mm	73.9	73.9	77.1	76.8
14 mm	73.9	73.4	76.7	76.7
16 mm	74.3	73.7	76.1	76.5
18 mm	74.5	74.3	75.5	76.1
Surface	74.6	75.1	75.7	78.2
Hardness Gradient	1.5	2.0	3.6	4.3

The hardness gradients, as seen in Table 3 above, range from 1.5 to 4.3 Shore C. These are shallow positive gradients and are determined by subtracting the hardness at the geometric center from the hardness at the surface of the core.

Cores formed from the same general formula as described above are also tested for the % cis-polybutadiene, % trans-polybutadiene, and % vinyl-polybutadiene. The results are presented below in Table 4.

TABLE 4

Core	% trans-PBR	% vinyl-PBR	% cis-PBR
Ex E outer surface	7.6	2.7	89.6
Ex E half radius	7.8	2.8	89.4
Ex E center	7.4	2.8	89.7
Ex F outer surface	9.2	2.7	88.4
Ex F half radius	13.2	2.6	85.4
Ex F center	8.5	2.9	88.6
Ex G outer surface	8.7	2.8	88.5
Ex G half radius	12.6	2.6	85.7
Ex G center	7.3	2.6	90.1

Cores E-G, above in TABLE 3, exhibit a shallow trans-polybutadiene gradient from core center to the surface.

The surface hardness of a core is obtained from the average of a number of measurements taken from opposing hemispheres of a core, taking care to avoid making measurements on the parting line of the core or on surface defects, such as holes or protrusions. Hardness measurements are made pursuant to ASTM D-2240 "Indentation Hardness of Rubber and Plastic by Means of a Durometer." Because of the curved surface of a core, care must be taken to insure that the core is centered under the durometer indenter before a surface hardness reading is obtained. A calibrated, digital durometer, capable of reading to 0.1 hardness units is used for all hardness measurements and is set to take hardness readings at 1 second after the maximum reading is obtained. The digital durometer must be attached to, and its foot made parallel to, the base of an automatic stand, such that the weight on the durometer and attack rate conform to ASTM D-2240.

To prepare a core for hardness gradient measurements, the core is gently pressed into a hemispherical holder having an internal diameter approximately slightly smaller than the diameter of the core, such that the core is held in place in the hemispherical portion of the holder while concurrently leaving the geometric central plane of the core exposed. The core is secured in the holder by friction, such that it will not move during the cutting and grinding steps, but the friction is not so excessive that distortion of the natural shape of the core would result. The core is secured such that the parting line of the core is roughly parallel to the top of the holder. The diameter of the core is measured 90 degrees to this orientation prior to securing. A measurement is also made from the bottom of the holder to the top of the core to provide a reference point for

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future calculations. A rough cut, made slightly above the exposed geometric center of the core using a band saw or other appropriate cutting tool, making sure that the core does not move in the holder during this step. The remainder of the core, still in the holder, is secured to the base plate of a surface grinding machine. The exposed 'rough' core surface is ground to a smooth, flat surface, revealing the geometric center of the core, which can be verified by measuring the height of the bottom of the holder to the exposed surface of the core, making sure that exactly half of the original height of the core, as measured above, has been removed to within ± 0.004 inches.

Leaving the core in the holder, the center of the core is found with a center square and carefully marked and the hardness is measured at the center mark. Hardness measurements at any distance from the center of the core may be measured by drawing a line radially outward from the center mark, and measuring and marking the distance from the center, typically in 2-mm increments. All hardness measurements performed on the plane passing through the geometric center are performed while the core is still in the holder and without having disturbed its orientation, such that the test surface is constantly parallel to the bottom of the holder. The hardness difference from any predetermined location on the core is calculated as the average surface hardness minus the hardness at the appropriate reference point, e.g., at the center of the core for single, solid core, such that a core surface softer than its center will have a negative hardness gradient.

Referring to TABLES 1-2, in Example 1, the surface is 10 Shore C points lower than the center hardness and 12 Shore C points lower than the hardest point in the core. In Example 3, the surface is 5 Shore C points lower than the center hardness and 8 Shore C points lower than the hardest point in the core. In Example 2, the center and surface hardness values are equal and the softest point in the core is 10 Shore C points lower than the surface.

In the examples of the invention presented in TABLE 1, the cure temperatures are varied from 305° F. to 320° F. and cure times are varied from 11 to 16 minutes. The core compositions of examples 1 and 2 are identical, and only the cure cycle is changed. In example 3 the amount of antioxidant is identical to examples 1 and 2, but other ingredients are varied as well the cure cycle. Additionally, the ratio of antioxidant to initiator varies from 0.50 to 0.57 from example 1 and 2 to example 3.

The ratio of antioxidant to initiator is one factor to control the surface hardness of the cores. The data shown in TABLE 2 shows that hardness gradient is at least, but not limited to, a function of the amount of antioxidant and peroxide, their ratio, and the cure cycle. It should be noted that higher antioxidant also requires higher peroxide initiator to maintain the desired compression.

The core of Comparative Example 1, whose composition is shown in TABLE 1 was cured using a conventional cure cycle, with a cure temperature of 350° F. and a cure time of 11 minutes. The inventive cores were produced using cure cycles of 305° F. for 14 minutes, 315° F. for 11 minutes and 320° F. for 16 minutes. The hardness gradients of these cores were measured and the following observations can be made. For the cores of the Comparative Examples, as expected, a conventional hard surface to soft center gradient can be clearly seen. The gradients for inventive cores follow substantially the same shape as one another.

In all preferred embodiments of invention, the hardness of the core at the surface is at most about the same as or substantially less than the hardness of the core at the center. Furthermore, the center hardness of the core may not be the

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hardest point in the core, but in all cases, it is preferred that it is at least equal to or harder than the surface. Additionally, the lowest hardness anywhere in the core does not have to occur at the surface. In some embodiments, the lowest hardness value occurs within about the outer 6 mm of the core surface. However, the lowest hardness value within the core can occur at any point from the surface, up to, but not including the center, as long as the surface hardness is still equal to, or less than the hardness of the center. It should be noted that in the present invention the formulation is the same throughout the core, or core layer, and no surface treatment is applied to the core to obtain the preferred surface hardness.

While the inventive golf ball may be formed from a variety of differing and conventional cover materials (both intermediate layer(s) and outer cover layer), preferred cover materials include, but are not limited to:

- (1) Polyurethanes, such as those prepared from polyols or polyamines and diisocyanates or polyisocyanates and/or their prepolymers, and those disclosed in U.S. Pat. Nos. 5,334,673 and 6,506,851;
- (2) Polyureas, such as those disclosed in U.S. Pat. Nos. 5,484,870 and 6,835,794; and
- (3) Polyurethane-urea hybrids, blends or copolymers comprising urethane or urea segments.

Suitable polyurethane compositions comprise a reaction product of at least one polyisocyanate and at least one curing agent. The curing agent can include, for example, one or more polyamines, one or more polyols, or a combination thereof. The polyisocyanate can be combined with one or more polyols to form a prepolymer, which is then combined with the at least one curing agent. Thus, the polyols described herein are suitable for use in one or both components of the polyurethane material, i.e., as part of a prepolymer and in the curing agent. Suitable polyurethanes are described in U.S. Patent Application Publication No. 2005/0176523, which is incorporated by reference in its entirety.

Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate (MDI); polymeric MDI; carbodiimide-modified liquid MDI; 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI); p-phenylene diisocyanate (PPDI); m-phenylene diisocyanate (MPDI); toluene diisocyanate (TDI); 3,3'-dimethyl-4,4'-biphenylene diisocyanate; isophoronediiisocyanate; 1,6-hexamethylene diisocyanate (HDI); naphthalene diisocyanate; xylene diisocyanate; p-tetramethylxylene diisocyanate; m-tetramethylxylene diisocyanate; ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate; tetracene diisocyanate; naphthalene diisocyanate; anthracene diisocyanate; isocyanurate of toluene diisocyanate; uretdione of hexamethylene diisocyanate; and mixtures thereof. Polyisocyanates are known to those of ordinary skill in the art as having more than one isocyanate group, e.g., di-isocyanate, tri-isocyanate, and tetra-isocyanate. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term MDI includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to

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have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer isocyanate groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI. The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 8.0% NCO, more preferably no greater than about 7.8%, and most preferably no greater than about 7.5% NCO with a level of NCO of about 7.2 or 7.0, or 6.5% NCO commonly used.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol. Examples include, but are not limited to, polytetramethylene ether glycol (PTMEG), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

In another embodiment, polyester polyols are included in the polyurethane material. Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol; polybutylene adipate glycol; polyethylene propylene adipate glycol; o-phthalate-1,6-hexanediol; poly(hexamethylene adipate) glycol; and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In another embodiment, polycaprolactone polyols are included in the materials of the invention. Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In yet another embodiment, polycarbonate polyols are included in the polyurethane material of the invention. Suitable polycarbonates include, but are not limited to, polyphthalate carbonate and poly(hexamethylene carbonate) glycol. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups. In one embodiment, the molecular weight of the polyol is from about 200 to about 4000.

Polyamine curatives are also suitable for use in the polyurethane composition of the invention and have been found to improve cut, shear, and impact resistance of the resultant balls. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene dianiline; m-phenylenediamine; 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-methylene-bis-(2,3-dichloroaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably,

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the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as ETHACURE® 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives, which include both primary and secondary amines, preferably have molecular weights ranging from about 64 to about 2000.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy) ethoxy]ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β-hydroxyethyl) ether; hydroquinone-di-(β-hydroxyethyl) ether; and mixtures thereof. Preferred hydroxy-terminated curatives include 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy) ethoxy]ethoxy]benzene; 1,4-butanediol, and mixtures thereof. Preferably, the hydroxy-terminated curatives have molecular weights ranging from about 48 to 2000. It should be understood that molecular weight, as used herein, is the absolute weight average molecular weight and would be understood as such by one of ordinary skill in the art.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

In a preferred embodiment of the present invention, saturated polyurethanes are used to form one or more of the cover layers, preferably the outer cover layer, and may be selected from among both castable thermoset and thermoplastic polyurethanes.

In this embodiment, the saturated polyurethanes of the present invention are substantially free of aromatic groups or moieties. Saturated polyurethanes suitable for use in the invention are a product of a reaction between at least one polyurethane prepolymer and at least one saturated curing agent. The polyurethane prepolymer is a product formed by a reaction between at least one saturated polyol and at least one saturated diisocyanate. As is well known in the art, that a catalyst may be employed to promote the reaction between the curing agent and the isocyanate and polyol, or the curing agent and the prepolymer.

Saturated diisocyanates which can be used include, without limitation, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene diisocyanate (HDI); 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; dicyclohexylmethane diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isophorone diisocyanate; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate. The most preferred saturated diisocyanates are 4,4'-dicyclohexylmethane diisocyanate and isophorone diisocyanate.

Saturated polyols which are appropriate for use in this invention include without limitation polyether polyols such as polytetramethylene ether glycol and poly(oxypropylene) glycol. Suitable saturated polyester polyols include polyeth-

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ylene adipate glycol, polyethylene propylene adipate glycol, polybutylene adipate glycol, polycarbonate polyol and ethylene oxide-capped polyoxypropylene diols. Saturated polycaprolactone polyols which are useful in the invention include diethylene glycol-initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, 1,6-hexanediol-initiated polycaprolactone; trimethylol propane-initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, and polytetramethylene ether glycol-initiated polycaprolactone. The most preferred saturated polyols are polytetramethylene ether glycol and PTMEG-initiated polycaprolactone.

Suitable saturated curatives include 1,4-butanediol, ethylene glycol, diethylene glycol, polytetramethylene ether glycol, propylene glycol; trimethanolpropane; tetra-(2-hydroxypropyl)-ethylenediamine; isomers and mixtures of isomers of cyclohexyldimethylol, isomers and mixtures of isomers of cyclohexane bis(methylamine); triisopropanolamine; ethylene diamine; diethylene triamine; triethylene tetramine; tetraethylene pentamine; 4,4'-dicyclohexylmethane diamine; 2,2,4-trimethyl-1,6-hexanediamine; 2,4,4-trimethyl-1,6-hexanediamine; diethyleneglycol di-(aminopropyl)ether; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,2-bis-(sec-butylamino)cyclohexane; 1,4-bis-(sec-butylamino)cyclohexane; isophorone diamine; hexamethylene diamine; propylene diamine; 1-methyl-2,4-cyclohexyl diamine; 1-methyl-2,6-cyclohexyl diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; imido-bispropylamine; isomers and mixtures of isomers of diaminocyclohexane; monoethanolamine; diethanolamine; triethanolamine; monoisopropanolamine; and diisopropanolamine. The most preferred saturated curatives are 1,4-butanediol, 1,4-cyclohexyldimethylol and 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

Alternatively, other suitable polymers include partially or fully neutralized ionomer, metallocene, or other single-site catalyzed polymer, polyester, polyamide, non-ionic thermoplastic elastomer, copolyether-esters, copolyether-amides, polycarbonate, polybutadiene, polyisoprene, polystyrene block copolymers (such as styrene-butadiene-styrene), styrene-ethylene-propylene-styrene, styrene-ethylene-butylene-styrene, and the like, and blends thereof. Thermosetting polyurethanes or polyureas are suitable for the outer cover layers of the golf balls of the present invention.

Additionally, polyurethane can be replaced with or blended with a polyurea material. Polyureas are distinctly different from polyurethane compositions, but also result in desirable aerodynamic and aesthetic characteristics when used in golf ball components. The polyurea-based compositions are preferably saturated in nature.

Without being bound to any particular theory, it is now believed that substitution of the long chain polyol segment in the polyurethane prepolymer with a long chain polyamine oligomer soft segment to form a polyurea prepolymer, improves shear, cut, and resiliency, as well as adhesion to other components. Thus, the polyurea compositions of this invention may be formed from the reaction product of an isocyanate and polyamine prepolymer crosslinked with a curing agent. For example, polyurea-based compositions of the invention may be prepared from at least one isocyanate, at least one polyether amine, and at least one diol curing agent or at least one diamine curing agent.

Any polyamine available to one of ordinary skill in the art is suitable for use in the polyurea prepolymer. Polyether amines are particularly suitable for use in the prepolymer. As used herein, "polyether amines" refer to at least polyoxyalkyleneamines containing primary amino groups attached to the terminus of a polyether backbone. Due to the rapid reaction of

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isocyanate and amine, and the insolubility of many urea products, however, the selection of diamines and polyether amines is limited to those allowing the successful formation of the polyurea prepolymers. In one embodiment, the polyether backbone is based on tetramethylene, propylene, ethylene, trimethylolpropane, glycerin, and mixtures thereof.

Suitable polyether amines include, but are not limited to, methyl-diethanolamine; polyoxyalkylenediamines such as, polytetramethylene ether diamines, polyoxypropylenetriamine, and polyoxypropylene diamines; poly(ethylene oxide capped oxypropylene) ether diamines; propylene oxide-based triamines; triethyleneglycoldiamines; trimethylolpropane-based triamines; glycerin-based triamines; and mixtures thereof. In one embodiment, the polyether amine used to form the prepolymer is JEFFAMINE® D2000 (manufactured by Huntsman Chemical Co. of Austin, Tex.).

The molecular weight of the polyether amine for use in the polyurea prepolymer may range from about 100 to about 5000. In one embodiment, the polyether amine molecular weight is about 200 or greater, preferably about 230 or greater. In another embodiment, the molecular weight of the polyether amine is about 4000 or less. In yet another embodiment, the molecular weight of the polyether amine is about 600 or greater. In still another embodiment, the molecular weight of the polyether amine is about 3000 or less. In yet another embodiment, the molecular weight of the polyether amine is between about 1000 and about 3000, and more preferably is between about 1500 to about 2500. Because lower molecular weight polyether amines may be prone to forming solid polyureas, a higher molecular weight oligomer, such as JEFFAMINE® D2000, is preferred.

As briefly discussed above, some amines may be unsuitable for reaction with the isocyanate because of the rapid reaction between the two components. In particular, shorter chain amines are fast reacting. In one embodiment, however, a hindered secondary diamine may be suitable for use in the prepolymer. Without being bound to any particular theory, it is believed that an amine with a high level of steric hindrance, e.g., a tertiary butyl group on the nitrogen atom, has a slower reaction rate than an amine with no hindrance or a low level of hindrance. For example, 4,4'-bis-(sec-butylamino)-dicyclohexylmethane (CLEARLINK® 1000) may be suitable for use in combination with an isocyanate to form the polyurea prepolymer.

Any isocyanate available to one of ordinary skill in the art is suitable for use in the polyurea prepolymer. Isocyanates for use with the present invention include aliphatic, cycloaliphatic, araliphatic, aromatic, any derivatives thereof, and combinations of these compounds having two or more isocyanate (NCO) groups per molecule. The isocyanates may be organic polyisocyanate-terminated prepolymers. The isocyanate-containing reactable component may also include any isocyanate-functional monomer, dimer, trimer, or multimeric adduct thereof, prepolymer, quasi-prepolymer, or mixtures thereof. Isocyanate-functional compounds may include monoisocyanates or polyisocyanates that include any isocyanate functionality of two or more.

Suitable isocyanate-containing components include diisocyanates having the generic structure: $O=C=N-R-N=C=O$, where R is preferably a cyclic, aromatic, or linear or branched hydrocarbon moiety containing from about 1 to about 20 carbon atoms. The diisocyanate may also contain one or more cyclic groups or one or more phenyl groups. When multiple cyclic or aromatic groups are present, linear and/or branched hydrocarbons containing from about 1 to about 10 carbon atoms can be present as spacers between the cyclic or aromatic groups. In some cases, the cyclic or aro-

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matic group(s) may be substituted at the 2-, 3-, and/or 4-positions, or at the ortho-, meta-, and/or para-positions, respectively. Substituted groups may include, but are not limited to, halogens, primary, secondary, or tertiary hydrocarbon groups, or a mixture thereof.

Examples of diisocyanates that can be used with the present invention include, but are not limited to, substituted and isomeric mixtures including 2,2', 2,4', and 4,4'-diphenylmethane diisocyanate; 3,3'-dimethyl-4,4'-biphenylene diisocyanate; toluene diisocyanate; polymeric MDI; carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate; para-phenylene diisocyanate; meta-phenylene diisocyanate; triphenyl methane-4,4'- and triphenyl methane-4,4'-triisocyanate; naphthylene-1,5-diisocyanate; 2,4', 4,4', and 2,2-biphenyl diisocyanate; polyphenyl polymethylene polyisocyanate; mixtures of MDI and PMDI; mixtures of PMDI and TDI; ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,2-diisocyanate; tetramethylene-1,3-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate; octamethylene diisocyanate; decamethylene diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl-cyclohexylene diisocyanate; 2,4-methylcyclohexane diisocyanate; 2,6-methylcyclohexane diisocyanate; 4,4'-dicyclohexyl diisocyanate; 2,4'-dicyclohexyl diisocyanate; 1,3,5-cyclohexane triisocyanate; isocyanatomethylcyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isocyanatoethylcyclohexane isocyanate; bis(isocyanatomethyl)-cyclohexane diisocyanate; 4,4'-bis(isocyanatomethyl)dicyclohexane; 2,4'-bis(isocyanatomethyl)dicyclohexane; isophorone diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate; 4,4'-dicyclohexylmethane diisocyanate; 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; 1,2-, 1,3-, and 1,4-phenylene diisocyanate; aromatic aliphatic isocyanate, such as 1,2-, 1,3-, and 1,4-xylene diisocyanate; meta-tetramethylxylene diisocyanate; para-tetramethylxylene diisocyanate; trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylxylene diisocyanate, isocyanurate of hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate, and mixtures thereof; dimerized urethane of any polyisocyanate, such as urethane of toluene diisocyanate, urethane of hexamethylene diisocyanate, and mixtures thereof; modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof.

Examples of saturated diisocyanates that can be used with the present invention include, but are not limited to, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate; octamethylene diisocyanate; decamethylene diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl-cyclohexylene diisocyanate; 2,4-methylcyclohexane diisocyanate; 2,6-methylcyclohexane diisocyanate; 4,4'-dicyclohexyl diisocyanate; 2,4'-dicyclohexyl diisocyanate; 1,3,5-cyclohexane triisocyanate; isocyanatomethylcyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isocyanatoethylcyclohexane isocyanate; bis(isocyanatomethyl)-cyclohexane diisocyanate; 4,4'-bis(isocyanatomethyl)dicyclohexane; 2,4'-bis(isocyanatomethyl)

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dicyclohexane; isophorone diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate; 4,4'-dicyclohexylmethane diisocyanate; 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; and mixtures thereof. Aromatic aliphatic isocyanates may also be used to form light stable materials. Examples of such isocyanates include 1,2-, 1,3-, and 1,4-xylene diisocyanate; meta-tetramethylxylene diisocyanate; para-tetramethylxylene diisocyanate; trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylxylene diisocyanate, isocyanurate of hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate, and mixtures thereof; dimerized urethane of any polyisocyanate, such as urethane of toluene diisocyanate, urethane of hexamethylene diisocyanate, and mixtures thereof; modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof. In addition, the aromatic aliphatic isocyanates may be mixed with any of the saturated isocyanates listed above for the purposes of this invention.

The number of unreacted NCO groups in the polyurea prepolymer of isocyanate and polyether amine may be varied to control such factors as the speed of the reaction, the resultant hardness of the composition, and the like. For instance, the number of unreacted NCO groups in the polyurea prepolymer of isocyanate and polyether amine may be less than about 14 percent. In one embodiment, the polyurea prepolymer has from about 5 percent to about 11 percent unreacted NCO groups, and even more preferably has from about 6 to about 9.5 percent unreacted NCO groups. In one embodiment, the percentage of unreacted NCO groups is about 3 percent to about 9 percent. Alternatively, the percentage of unreacted NCO groups in the polyurea prepolymer may be about 7.5 percent or less, and more preferably, about 7 percent or less. In another embodiment, the unreacted NCO content is from about 2.5 percent to about 7.5 percent, and more preferably from about 4 percent to about 6.5 percent.

When formed, polyurea prepolymers may contain about 10 percent to about 20 percent by weight of the prepolymer of free isocyanate monomer. Thus, in one embodiment, the polyurea prepolymer may be stripped of the free isocyanate monomer. For example, after stripping, the prepolymer may contain about 1 percent or less free isocyanate monomer. In another embodiment, the prepolymer contains about 0.5 percent by weight or less of free isocyanate monomer.

The polyether amine may be blended with additional polyols to formulate copolymers that are reacted with excess isocyanate to form the polyurea prepolymer. In one embodiment, less than about 30 percent polyol by weight of the copolymer is blended with the saturated polyether amine. In another embodiment, less than about 20 percent polyol by weight of the copolymer, preferably less than about 15 percent by weight of the copolymer, is blended with the polyether amine. The polyols listed above with respect to the polyurethane prepolymer, e.g., polyether polyols, polycaprolactone polyols, polyester polyols, polycarbonate polyols, hydrocarbon polyols, other polyols, and mixtures thereof, are also suitable for blending with the polyether amine. The molecular weight of these polymers may be from about 200 to about 4000, but also may be from about 1000 to about 3000, and more preferably are from about 1500 to about 2500.

The polyurea composition can be formed by crosslinking the polyurea prepolymer with a single curing agent or a blend of curing agents. The curing agent of the invention is preferably an amine-terminated curing agent, more preferably a secondary diamine curing agent so that the composition contains only urea linkages. In one embodiment, the amine-

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terminated curing agent may have a molecular weight of about 64 or greater. In another embodiment, the molecular weight of the amine-curing agent is about 2000 or less. As discussed above, certain amine-terminated curing agents may be modified with a compatible amine-terminated freezing point depressing agent or mixture of compatible freezing point depressing agents.

Suitable amine-terminated curing agents include, but are not limited to, ethylene diamine; hexamethylene diamine; 1-methyl-2,6-cyclohexyl diamine; tetrahydroxypropylene ethylene diamine; 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 4,4'-dicyclohexylmethane diamine; 1,4-cyclohexane-bis-(methylamine); 1,3-cyclohexane-bis-(methylamine); diethylene glycol di-(aminopropyl) ether; 2-methylpentamethylene-diamine; diaminocyclohexane; diethylene triamine; triethylene tetramine; tetraethylene pentamine; propylene diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; dipropylene triamine; imido-bis-propylamine; monoethanolamine, diethanolamine; triethanolamine; monoisopropanolamine, diisopropanolamine; isophoronediamine; 4,4'-methylenebis-(2-chloroaniline); 3,5-dimethylthio-2,4-toluenediamine; 3,5-dimethylthio-2,6-toluenediamine; 3,5-diethylthio-2,4-toluenediamine; 3,5-diethylthio-2,6-toluenediamine; 4,4'-bis-(sec-butylamino)-diphenylmethane and derivatives thereof; 1,4-bis-(sec-butylamino)-benzene; 1,2-bis-(sec-butylamino)-benzene; N,N'-dialkylamino-diphenylmethane; N,N,N',N'-tetrakis(2-hydroxypropyl) ethylene diamine; trimethyleneglycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; 4,4'-methylenebis-(3-chloro-2,6-diethylenylaniline); 4,4'-methylenebis-(2,6-diethylaniline); meta-phenylenediamine; paraphenylenediamine; and mixtures thereof. In one embodiment, the amine-terminated curing agent is 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

Suitable saturated amine-terminated curing agents include, but are not limited to, ethylene diamine; hexamethylene diamine; 1-methyl-2,6-cyclohexyl diamine; tetrahydroxypropylene ethylene diamine; 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 4,4'-dicyclohexylmethane diamine; 4,4'-methylenebis-(2,6-diethylaminocyclohexane); 1,4-cyclohexane-bis-(methylamine); 1,3-cyclohexane-bis-(methylamine); diethylene glycol di-(aminopropyl) ether; 2-methylpentamethylene-diamine; diaminocyclohexane; diethylene triamine; triethylene tetramine; tetraethylene pentamine; propylene diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; imido-bis-propylamine; monoethanolamine, diethanolamine; triethanolamine; monoisopropanolamine, diisopropanolamine; isophoronediamine; triisopropanolamine; and mixtures thereof. In addition, any of the polyether amines listed above may be used as curing agents to react with the polyurea prepolymers.

Cover layers of the inventive golf ball may also be formed from ionomeric polymers, preferably highly-neutralized ionomers (HNP). In a preferred embodiment, at least one intermediate layer of the golf ball is formed from an HNP material or a blend of HNP materials. The acid moieties of the HNP's, typically ethylene-based ionomers, are preferably neutralized greater than about 70%, more preferably greater than about 90%, and most preferably at least about 100%. The

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HNP's can also be blended with a second polymer component, which, if containing an acid group, may be neutralized in a conventional manner, by the organic fatty acids of the present invention, or both. The second polymer component, which may be partially or fully neutralized, preferably comprises ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, polyamides, polycarbonates, polyesters, polyurethanes, polyureas, thermoplastic elastomers, polybutadiene rubber, balata, metallocene-catalyzed polymers (grafted and non-grafted), single-site polymers, high-crystalline acid polymers, cationic ionomers, and the like. HNP polymers typically have a material hardness of between about 20 and about 80 Shore D, and a flexural modulus of between about 3,000 psi and about 200,000 psi.

In one embodiment of the present invention the HNP's are ionomers and/or their acid precursors that are preferably neutralized, either fully or partially, with organic acid copolymers or the salts thereof. The acid copolymers are preferably α -olefin, such as ethylene, C₃₋₈ α , β -ethylenically unsaturated carboxylic acid, such as acrylic and methacrylic acid, copolymers. They may optionally contain a softening monomer, such as alkyl acrylate and alkyl methacrylate, wherein the alkyl groups have from 1 to 8 carbon atoms.

The acid copolymers can be described as E/X/Y copolymers where E is ethylene, X is an α , β -ethylenically unsaturated carboxylic acid, and Y is a softening comonomer. In a preferred embodiment, X is acrylic or methacrylic acid and Y is a C₁₋₈ alkyl acrylate or methacrylate ester. X is preferably present in an amount from about 1 to about 35 weight percent of the polymer, more preferably from about 5 to about 30 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer. Y is preferably present in an amount from about 0 to about 50 weight percent of the polymer, more preferably from about 5 to about 25 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer.

Specific acid-containing ethylene copolymers include, but are not limited to, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/acrylic acid/ethyl acrylate, ethylene/methacrylic acid/ethyl acrylate, and ethylene/acrylic acid/methyl acrylate copolymers. The most preferred acid-containing ethylene copolymers are, ethylene/(meth) acrylic acid/n-butyl, acrylate, ethylene/(meth) acrylic acid/ethyl acrylate, and ethylene/(meth) acrylic acid/methyl acrylate copolymers.

Ionomers are typically neutralized with a metal cation, such as Li, Na, Mg, K, Ca, or Zn. It has been found that by adding sufficient organic acid or salt of organic acid, along with a suitable base, to the acid copolymer or ionomer, however, the ionomer can be neutralized, without losing processability, to a level much greater than for a metal cation. Preferably, the acid moieties are neutralized greater than about 80%, preferably from 90-100%, most preferably 100% without losing processability. This accomplished by melt-blending an ethylene α , β -ethylenically unsaturated carboxylic acid copolymer, for example, with an organic acid or a salt of organic acid, and adding a sufficient amount of a cation source to increase the level of neutralization of all the acid

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moieties (including those in the acid copolymer and in the organic acid) to greater than 90%, (preferably greater than 100%).

The organic acids of the present invention are aliphatic, mono- or multi-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. The salts of organic acids of the present invention include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, salts of fatty acids, particularly stearic, behenic, erucic, oleic, linoelic or dimerized derivatives thereof. It is preferred that the organic acids and salts of the present invention be relatively non-migratory (they do not bloom to the surface of the polymer under ambient temperatures) and non-volatile (they do not volatilize at temperatures required for melt-blending).

The ionomers of the invention may also be more conventional ionomers, i.e., partially-neutralized with metal cations. The acid moiety in the acid copolymer is neutralized about 1 to about 90%, preferably at least about 20 to about 75%, and more preferably at least about 40 to about 70%, to form an ionomer, by a cation such as lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum, or a mixture thereof.

In a preferred embodiment, the inventive single-layer core is enclosed with two cover layers, where the inner cover layer has a thickness of about 0.01 inches to about 0.06 inches, more preferably about 0.015 inches to about 0.040 inches, and most preferably about 0.02 inches to about 0.035 inches, and the inner cover layer is formed from a partially- or fully-neutralized ionomer having a Shore D hardness of greater than about 55, more preferably greater than about 60, and most preferably greater than about 65. In this embodiment, the outer cover layer should have a thickness of about 0.015 inches to about 0.055 inches, more preferably about 0.02 inches to about 0.04 inches, and most preferably about 0.025 inches to about 0.035 inches, and has a hardness of about Shore D 60 or less, more preferably 55 or less, and most preferably about 52 or less. The inner cover layer should be harder than the outer cover layer. In this embodiment the outer cover layer comprises a partially- or fully-neutralized ionomer, a polyurethane, polyurea, or blend thereof. A most preferred outer cover layer is a castable or reaction injection molded polyurethane, polyurea or copolymer or hybrid thereof having a Shore D hardness of about 40 to about 50. A most preferred inner cover layer material is a partially-neutralized ionomer comprising a zinc, sodium or lithium neutralized ionomer such as SURLYN® 8940, 8945, 9910, 7930, 7940, or blend thereof having a Shore D hardness of about 63 to about 68.

In another multi-layer cover, single core embodiment, the outer cover and inner cover layer materials and thickness are the same but, the hardness range is reversed, that is, the outer cover layer is harder than the inner cover layer.

In an alternative preferred embodiment, the golf ball is a one-piece golf ball having a dimpled surface and having a surface hardness equal to or less than the center hardness (i.e., a negative hardness gradient). The one-piece ball preferably has a diameter of about 1.680 inches to about 1.690 inches, a weight of about 1.620 oz, an Atti compression of from about 40 to 120, and a COR of about 0.750 to 0.825.

In a preferred two-piece ball embodiment, the single-layer core having a negative hardness gradient is enclosed with a single layer of cover material having a Shore D hardness of from about 20 to about 80, more preferably about 40 to about 75 and most preferably about 45 to about 70, and comprises a

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thermoplastic or thermosetting polyurethane, polyurea, polyamide, polyester, polyester elastomer, polyether-amide or polyester-amide, partially or fully neutralized ionomer, polyolefin such as polyethylene, polypropylene, polyethylene copolymers such as ethylene-butyl acrylate or ethylene-methyl acrylate, poly(ethylene methacrylic acid) co- and terpolymers, metallocene-catalyzed polyolefins and polar-group functionalized polyolefins and blends thereof. A preferred cover material in the two-piece embodiment is an ionomer (either conventional or HNP) having a hardness of about 50 to about 70 Shore D. Another preferred cover material in the two-piece embodiment is a thermoplastic or thermosetting polyurethane or polyurea. A preferred ionomer is a high acid ionomer comprising a copolymer of ethylene and methacrylic or acrylic acid and having an acid content of at least 16 to about 25 weight percent. In this case the reduced spin contributed by the relatively rigid high acid ionomer may be offset to some extent by the spin-increasing negative gradient core. The core may have a diameter of about 1.0 inch to about 1.64 inches, preferably about 1.30 inches to about 1.620, and more preferably about 1.40 inches to about 1.60 inches.

A preferred ionomer for the cover layers of the invention is a high acid ionomer comprising a copolymer of ethylene and methacrylic or acrylic acid and having an acid content of at least 16 to about 25 weight percent (wt. %). As used herein, the terms "high-acid ionomer" and "high-acid copolymer" are defined as an acid copolymer or its ionomer derivatives which contains at least about 16 wt. % acid, preferably from about 16 wt. % to about 25 wt. % acid, more preferably from about 18 wt. % to about 22 wt. % acid and most preferably about 18.5 wt. % acid to about 21 wt. % acid, where about 10 to 90 percent of the acid is partially-neutralized with sodium, manganese, lithium, potassium, zinc, magnesium, calcium or nickel ions. High-acid ionomers are commercially-available from DuPont under the tradename SURLYN®. Examples of suitable high acid ionomers include SURLYN® 8546 (neutralized with Li cations), SURLYN® 8150 (neutralized with Na cations), SURLYN® 9120 (neutralized with Zn cations), and SURLYN® 9150 (neutralized with Zn cations)—each of these SURLYN® materials comprises about 19 wt. % methacrylic acid. Other suitable high-acid copolymers include those commercially-available from A. Schulman under the tradename CLARIX®, and high-acid ionomers neutralized using Dow 5800 Series ethylene-acrylic acid.

In a preferred embodiment, the cover is a two-layer structure including an inner cover layer and an outer cover layer. The outer cover comprises a polyurethane (or polyurea) material as described above. The inner cover layer, or casing layer, comprises a high-acid ionomer material described above. The high-acid ionomers of the invention preferably comprise greater than about 16 wt. % acid, more preferably greater than about 18 wt. % acid, and most preferably about 18.5 wt. % acid to about 21 wt. % acid. The most preferred blends include blends of Li/Na/Zn high-acid ionomers and blends of Na/Zn high-acid ionomers. In a few preferred embodiments, the casing layer can comprise a 50/50 blend of SURLYN® 8546 and SURLYN® 9150, a 50/50 blend of SURLYN® 8150 and SURLYN® 9120, or a 75/25 blend of AD 8546 and AD 9945 (a low-acid ionomer). Other blends of high-acid ionomers and low-acid ionomers are envisioned.

In these embodiments, the outer cover layer preferably comprises a polyurethane material that has an isocyanate (NCO) content of about 5 percent to about 7 percent NCO, more preferably about 5.5 percent to about 6.6 percent NCO, and most preferably about 5.9 percent to about 6.2 percent NCO. The outer cover has a material (button) hardness of

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about 35 Shore D to about 55 Shore D, more preferably about 38 Shore D to about 52 Shore D, and most preferably about 40 Shore D or 42 Shore D to about 46 Shore D to 48 Shore D. In one embodiment, the cover comprises about 3 wt. % to about 5 wt. % of a UV stabilizer, preferably a TINUVIN® UV stabilizer, such as TINUVIN® 328. More preferably the UV stabilizer is present at about 3.8 wt. % to about 4.2 wt. %.

Other suitable ionomers include those listed in TABLE 5 below.

TABLE 5

Ionomers	Cation	wt % acid	Mole % Neutralization	Melt Flow Index	Shore D Hardness
SURLYN ® 7940	Lithium	15.0 MAA	42	2.6	68
SURLYN ® 8940	Sodium	15.0 MAA	30	2.8	65
SURLYN ® 8945	Sodium	15.0 MAA	51	4.5	65
SURLYN ® 9910	Zinc	15.0 MAA	61	0.7	65
SURLYN ® 9945	Zinc	15.0 MAA	54	4.2	55
SURLYN ® 6120	Magnesium	19.0 MAA	39	1.1	67
SURLYN ® 8140	Sodium	19.0 MAA	37	2.6	68
SURLYN ® 8150	Sodium	19.0 MAA	45	4.5	68
SURLYN ® 9120	Zinc	19.0 MAA	36	1.3	66
SURLYN ® 9150	Zinc	19.0 MAA	38	4.5	65
SURLYN ® AD 8546	Lithium	19.0 MAA	44	1.1	70
SURLYN ® AD 1092	Magnesium	19.0 MAA	—	2.8	67
CLARIX ® 211702-01	Zinc	17.0 AA	—	2.0	66
CLARIX ® 411701-01	Magnesium	17.0 AA	—	2.0	66
CLARIX ® 11710-01	Sodium	17.0 AA	—	10.0	67
CLARIX ® 511704-01	Lithium	17.0 AA	—	3.5	67
CLARIX ® 611701-01	Potassium	17.0 AA	—	1.0	67
Acid Copolymers					
PRIMACOR ® 5985	NA	20.5 AA	0	240	—
PRIMACOR ® 5986	NA	20.5 AA	0	300	—
PRIMACOR ® 5980i	NA	20.5 AA	0	300	—
PRIMACOR ® 5990i	NA	20.0 AA	0	1,300	—
Dow XUS ® 60751.17	NA	19.8 AA	0	600	—
Dow XUS ® 60753.02L	NA	17.0 AA	0	60	—

Melt Flow Index is measured at 190° C. and the units are g/10 min

Shore D hardness is material hardness measured on a 10-day aged button

SURLYN ® materials are commercially available from DuPont, CLARIX ® resins are commercially available from A. Schulman, and PRIMACOR ® acid copolymers and XUS ® copolymers are sold by Dow Chemical Co.

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parting line configuration of said pattern may be either a straight line or a staggered wave parting line (SWPL). More preferably the dimple number is 330, 332, or 392 and comprises 5 to 7 dimples sizes and the parting line is a SWPL. In a most preferred embodiment, the dimple pattern has 328 dimples arranged in a tetrahedron pattern and the parting line is a SWPL.

In any of these embodiments the single-layer core may be replaced with a 2 or more layer core wherein at least one core

The core (dual) may have any diameter, but is about 1.0 inch to about 1.64 inches, preferably about 1.30 inches to about 1.620, more preferably about 1.40 inches to about 1.60 inches, and most preferably about 1.50 inches to about 1.56 inches, such as 1.51 inches, 1.52 inches, 1.53 inches, 1.54 inches, or 1.5 inches. The dual core preferably has a positive hardness gradient but, in an alternative embodiment, may also have a negative hardness gradient. The preferred embodiment is a dual core having a center with a zero or negative hardness gradient surrounded by an outer core layer such that the dual core has an overall positive hardness gradient of about 10 to 20, most preferably about 15 to 20.

Another preferred cover material comprises a castable or reaction injection moldable polyurethane, polyurea, or copolymer or hybrid of polyurethane/polyurea. Preferably, this cover is thermosetting but may be a thermoplastic, having a Shore D hardness of about 20 to about 70, more preferably about 30 to about 65 and most preferably about 35 to about 60. A moisture vapor barrier layer, such as disclosed in U.S. Pat. Nos. 6,632,147; 6,932,720; 7,004,854; and 7,182,702, all of which are incorporated by reference herein in their entirety, are optionally employed between the cover layer and the core.

While any of the embodiments herein may have any known dimple number and pattern, a preferred number of dimples is 252 to 456, and more preferably is 330 to 392. The dimples may comprise any width, depth, and edge angle disclosed in the prior art and the patterns may comprises multitudes of dimples having different widths, depths and edge angles. The

layer has a negative hardness gradient. Other than in the operating examples, or unless otherwise expressly specified, all of the numerical ranges, amounts, values and percentages such as those for amounts of materials and others in the specification may be read as if prefaced by the word “about” even though the term “about” may not expressly appear with the value, amount or range. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Furthermore, when numerical ranges of varying scope are set forth herein, it is contemplated that any combination of these values inclusive of the recited values may be used.

While it is apparent that the illustrative embodiments of the invention disclosed herein fulfill the objective stated above, it is appreciated that numerous modifications and other

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embodiments may be devised by those skilled in the art. Therefore, it will be understood that the appended claims are intended to cover all such modifications and embodiments, which would come within the spirit and scope of the present invention.

What is claimed is:

1. A golf ball comprising:
 - an inner core layer having an outer surface and a geometric center and being formed from a substantially homogeneous rubber composition;
 - an outer core layer disposed about the inner core layer to form a dual core;
 - an inner cover layer disposed about the dual core, the inner cover comprising a high-acid ionomer and having a material hardness of about 66 to 75 Shore D, the high-acid ionomer having an acid content of about 16% or greater; and
 - an outer cover layer disposed about the inner cover layer, the outer cover comprising a polyurethane and having a material hardness of about 38 Shore D to about 56 Shore D;
 wherein the inner core surface hardness is greater than the geometric center hardness by about 1 to 10 Shore C to define a shallow positive hardness gradient; and wherein the dual core surface hardness is at least about 85 Shore C.
2. The golf ball of claim 1, wherein the positive hardness gradient is about 1 to 5 Shore C.
3. The golf ball of claim 1, wherein the positive hardness gradient is about 2 to 8 Shore C.
4. The golf ball of claim 3, wherein the positive hardness gradient is about 2.5 to 7 Shore C.
5. The golf ball of claim 1, wherein the ionomer has an acid content of about 18.5% to about 21.5%.
6. The golf ball of claim 1, wherein the dual core has an outer diameter of about 1.45 to about 1.62 inches.
7. The golf ball of claim 6, wherein the dual core has an outer diameter of about 1.50 to about 1.58 inches.
8. A golf ball comprising:
 - an inner core layer having an outer surface and a geometric center and being formed from a substantially homogeneous rubber composition;

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an outer core layer disposed about the inner core layer to form a dual core;

an inner cover layer disposed about the dual core, the inner cover comprising a high-acid ionomer and having a material hardness of about 66 to 75 Shore D, the high-acid ionomer having an acid content of about 16% or greater; and

an outer cover layer disposed about the inner cover layer, the outer cover comprising a polyurethane and having a material hardness of about 38 Shore D to about 56 Shore D;

wherein the inner core surface hardness is greater than the geometric center hardness by about 1 to 10 Shore C to define a shallow positive hardness gradient; and wherein the hardness of the outer surface of the dual core is about 15 Shore C or greater than the hardness at the geometric center.

9. A golf ball comprising:

an inner core layer having an outer surface and a geometric center and being formed from a substantially homogeneous rubber composition;

an outer core layer disposed about the inner core layer to form a dual core;

an inner cover layer disposed about the dual core, the inner cover comprising a high-acid ionomer and having a material hardness of about 66 to 75 Shore D, the high-acid ionomer having an acid content of about 16% or greater; and

an outer cover layer disposed about the inner cover layer, the outer cover comprising a polyurethane and having a material hardness of about 38 Shore D to about 56 Shore D;

wherein the inner core surface hardness is greater than the geometric center hardness by about 1 to 10 Shore C to define a shallow positive hardness gradient; and wherein the hardness of the outer surface of the dual core is about 15 Shore C to about 20 Shore C greater than the hardness at the geometric center.

* * * * *

Exhibit G



US006358161B1

(12) **United States Patent**
Aoyama

(10) **Patent No.:** **US 6,358,161 B1**
(45) **Date of Patent:** **Mar. 19, 2002**

(54) **GOLF BALL DIMPLE PATTERN**

(75) Inventor: **Steven Aoyama**, Marion, MA (US)

(73) Assignee: **Acushnet Company**, Fairhaven, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/404,164**

(22) Filed: **Sep. 27, 1999**

Related U.S. Application Data

(62) Division of application No. 08/922,633, filed on Sep. 3, 1997, now Pat. No. 5,957,786.

(51) **Int. Cl.**⁷ **A63B 37/14**

(52) **U.S. Cl.** **473/383**

(58) **Field of Search** 473/377-384

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Primary Examiner—Mark S. Graham

Assistant Examiner—Raeann Gorden

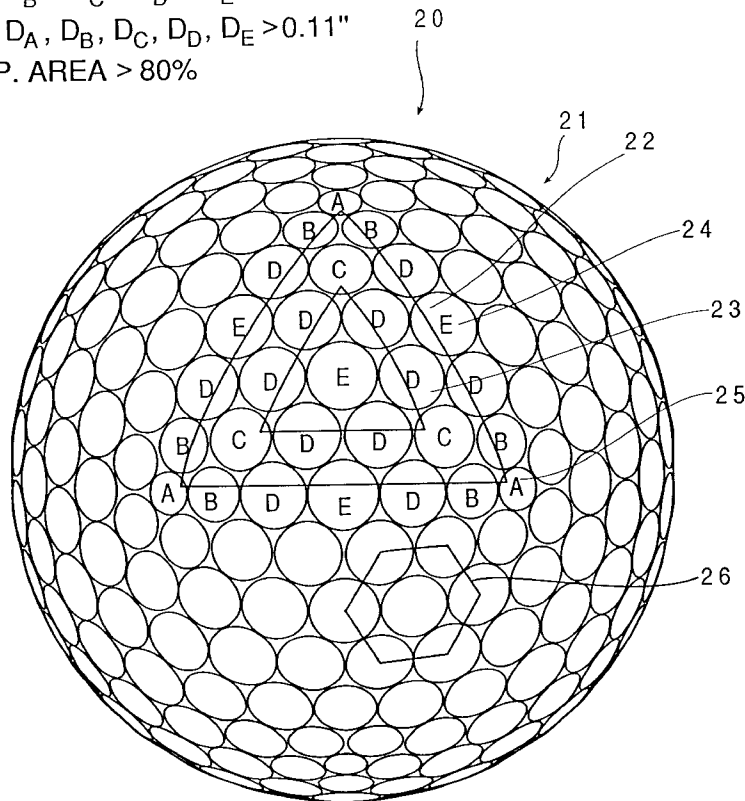
(74) *Attorney, Agent, or Firm*—Swidler Berlin Shereff Friedman, LLP

(57) **ABSTRACT**

A golf ball having an outside surface with a plurality of dimples formed thereon, wherein at least about 80% of the dimples have a diameter of about 0.11 inches or greater and the dimples cover more than 80% of the outer-surface.

19 Claims, 9 Drawing Sheets

$D_A < D_B \leq D_C \leq D_D \leq D_E$
80% $D_A, D_B, D_C, D_D, D_E > 0.11"$
DIMP. AREA > 80%



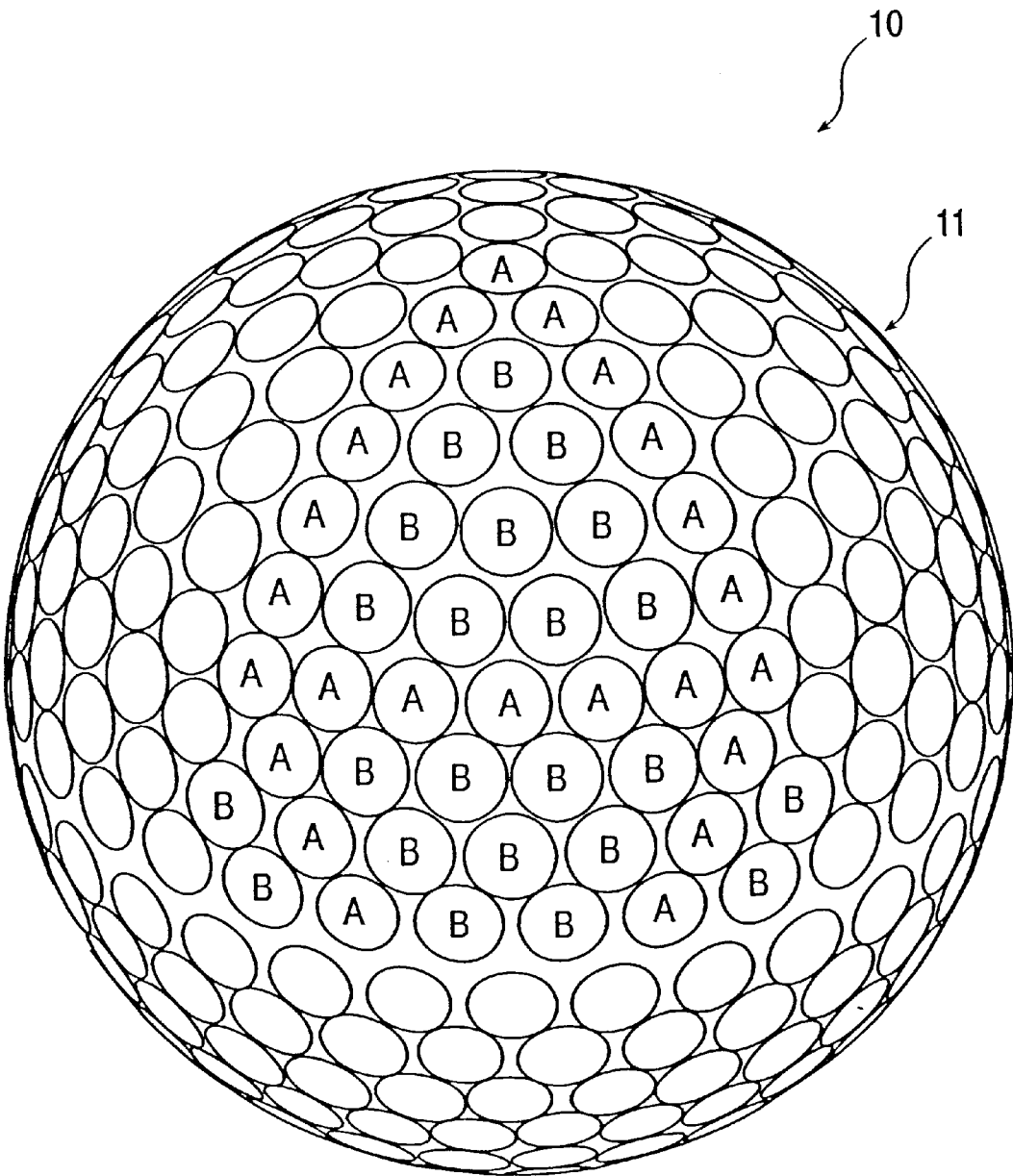


FIG. 1
PRIOR ART

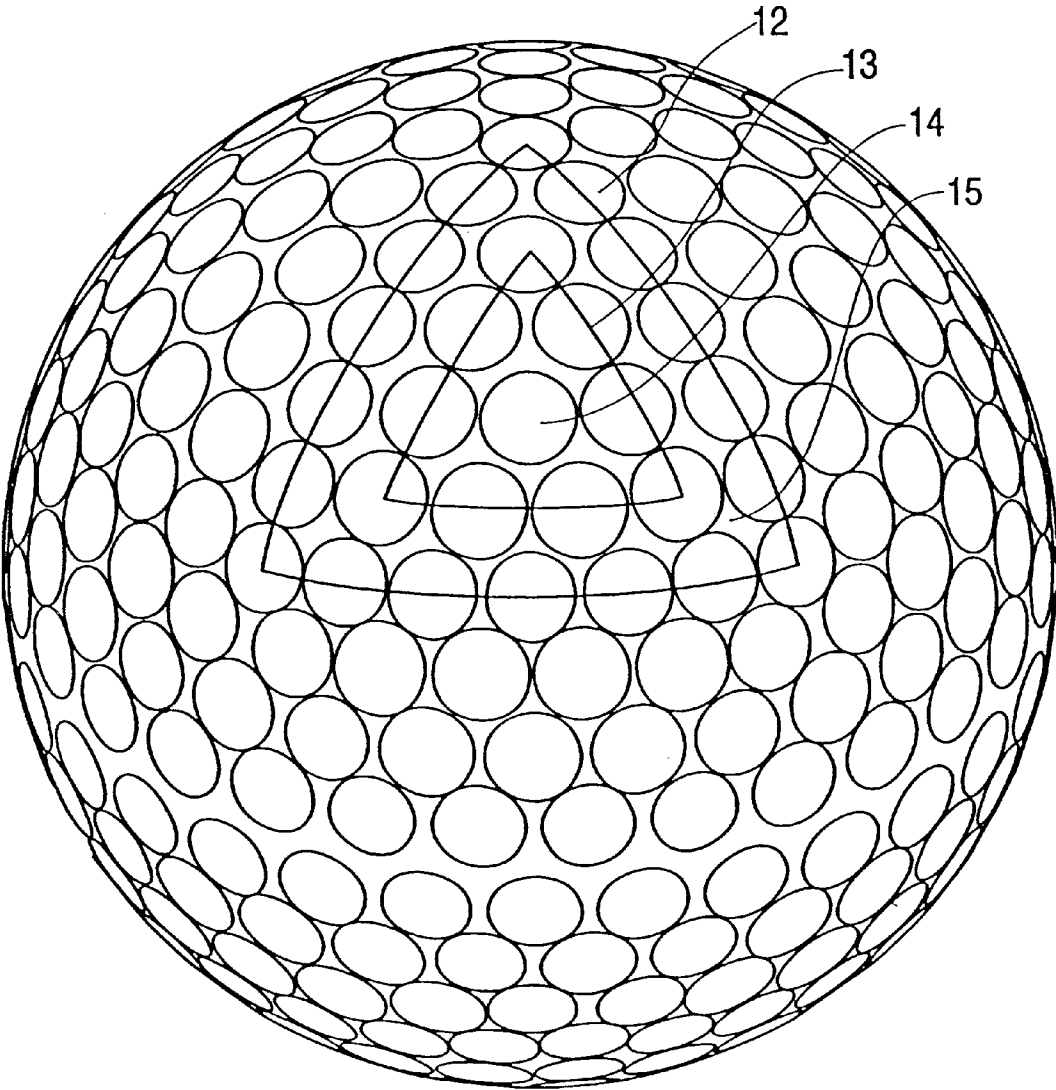


FIG. 2
PRIOR ART

$$D_A < D_B \leq D_C \leq D_D \leq D_E$$

$$80\% D_A, D_B, D_C, D_D, D_E > 0.11''$$

$$\text{DIMP. AREA} > 80\%$$

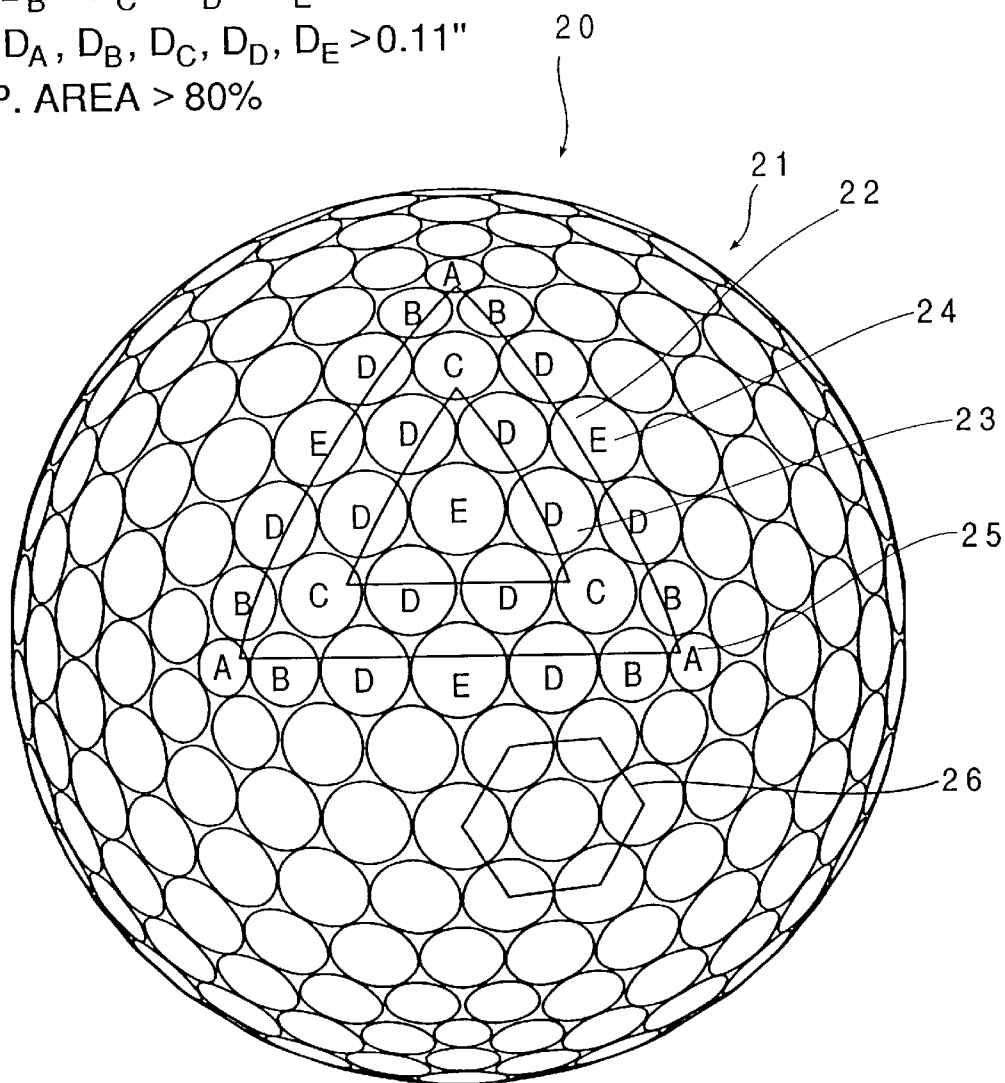


Fig. 3

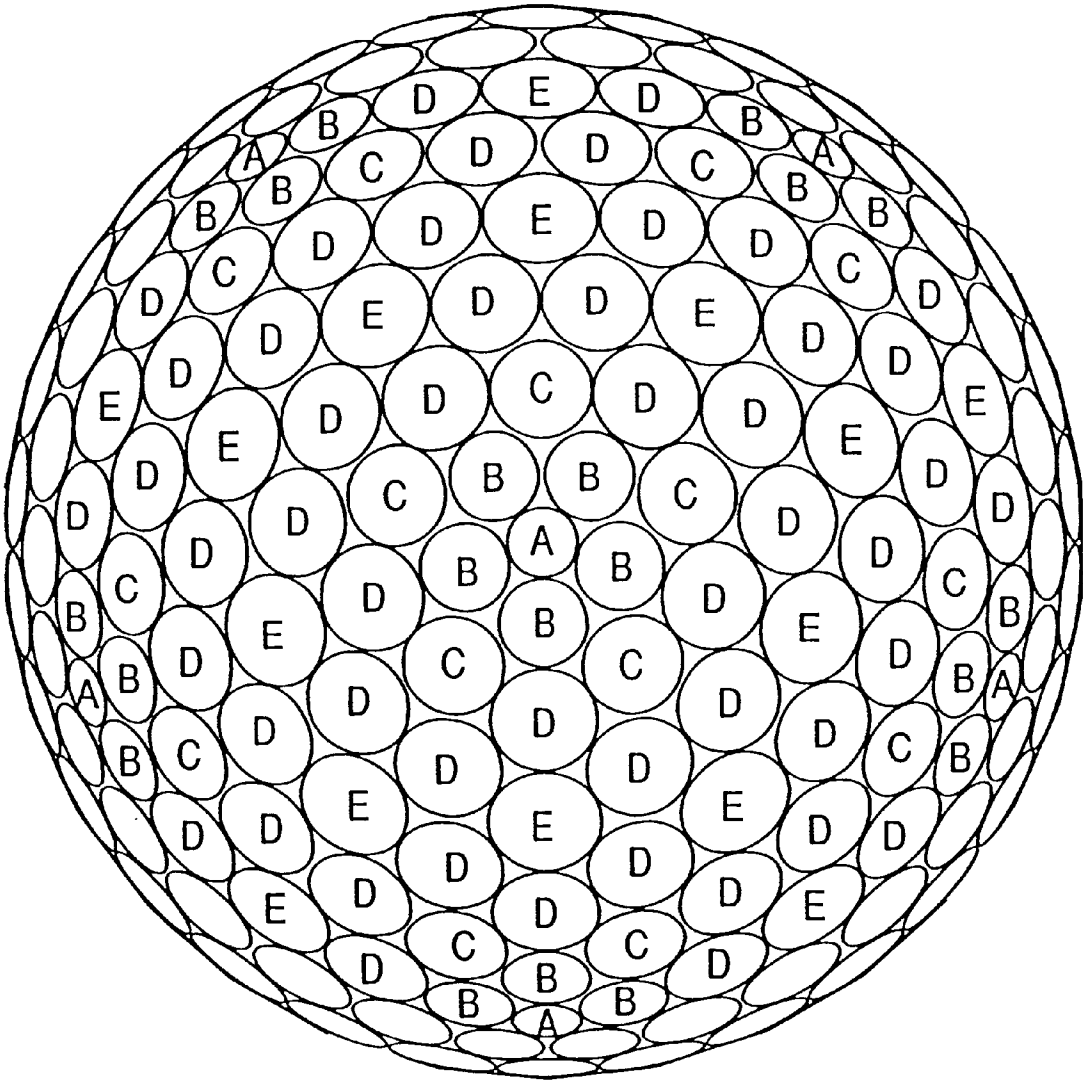


FIG. 4

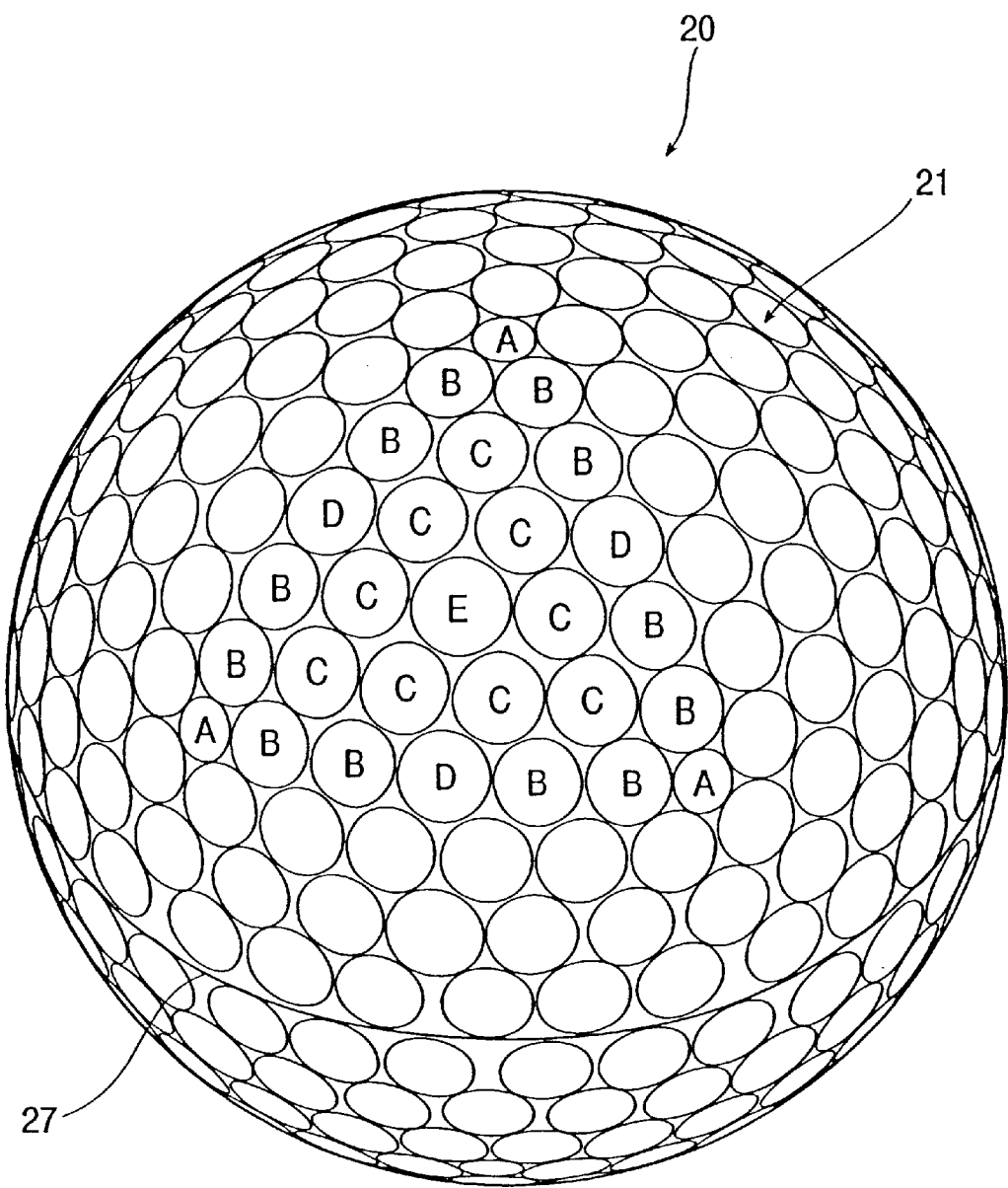


FIG. 5

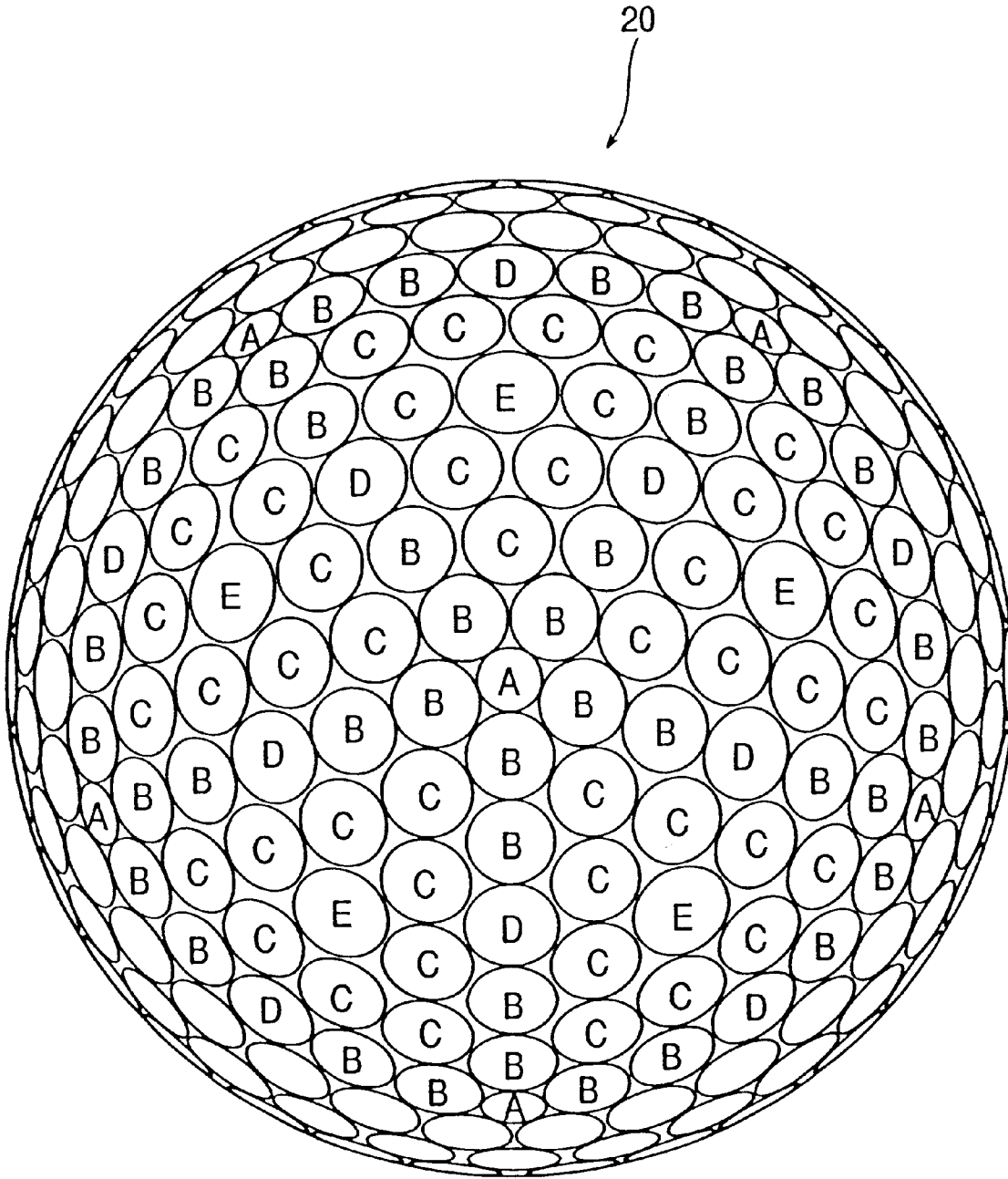


FIG. 6

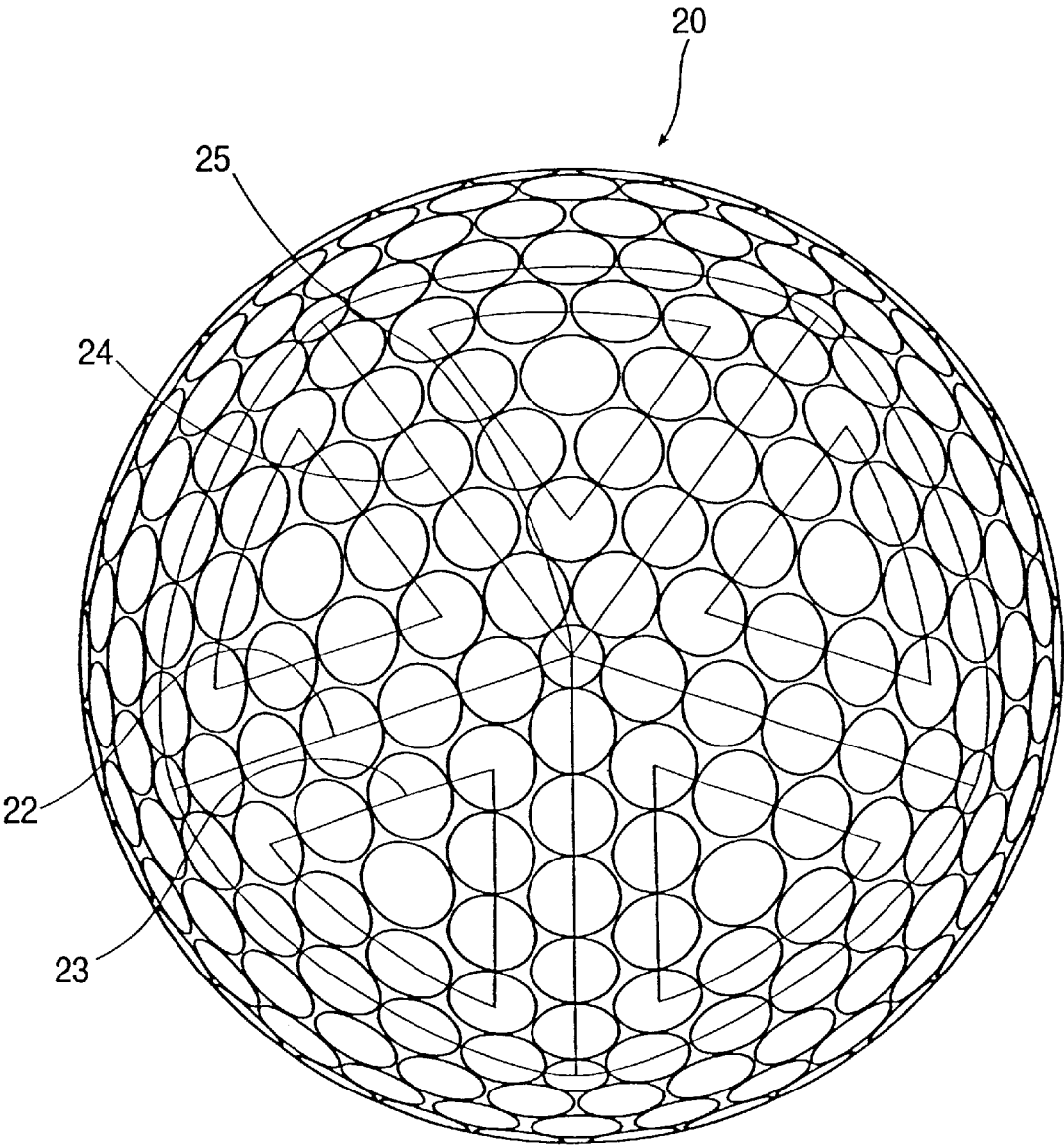


FIG. 7

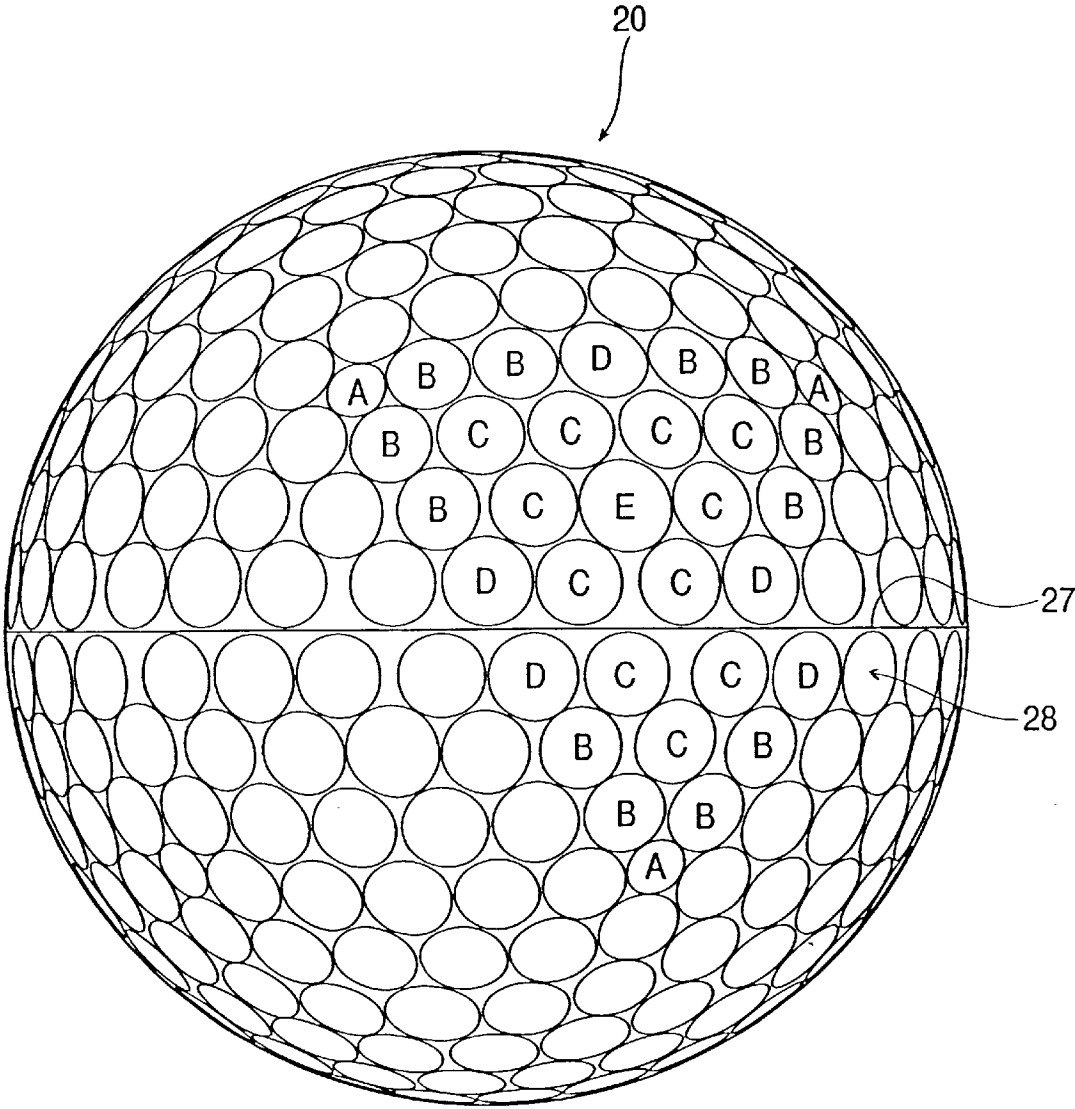


FIG. 8

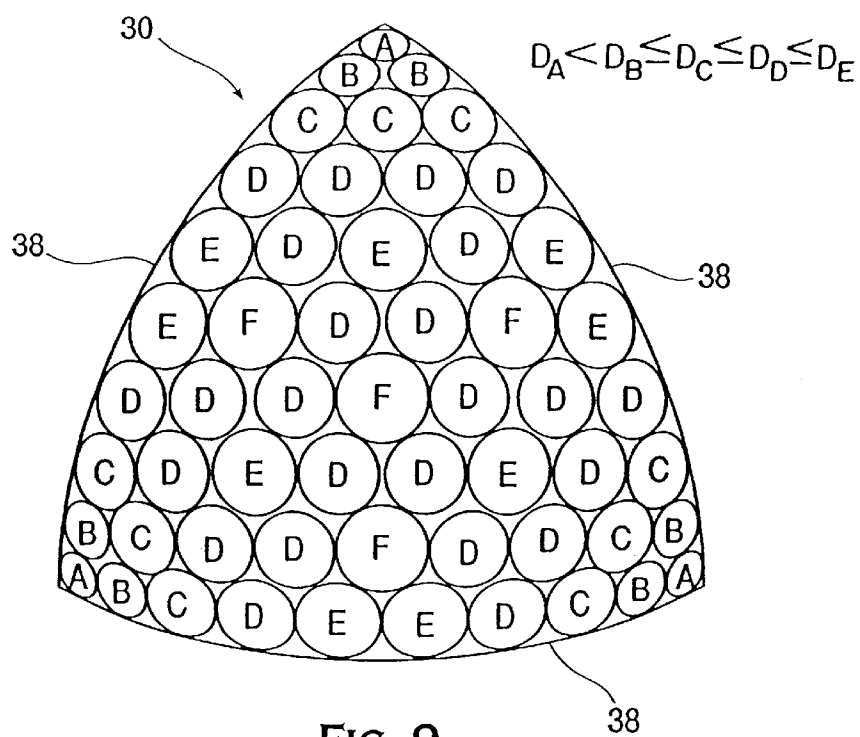


FIG. 9

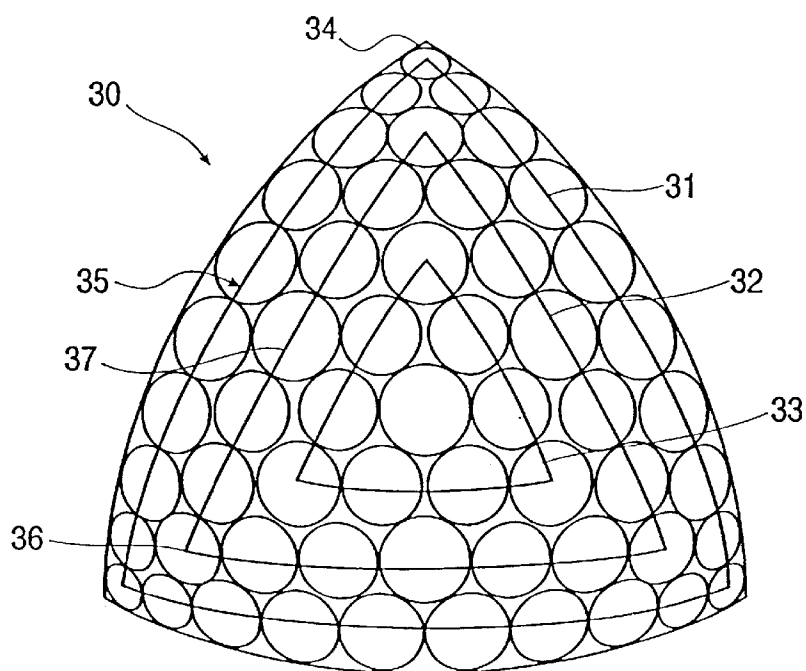


FIG. 10

US 6,358,161 B1

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GOLF BALL DIMPLE PATTERN**CROSS-REFERENCE TO RELATED APPLICATION**

This is a division of application Ser. No. 08/922,633, filed Sept. 3, 1997, Now Pat. 5,957,786.

BACKGROUND OF THE INVENTION

The present invention is directed to a golf ball and, more particularly, a golf ball having an improved dimple pattern.

Golf balls were originally made with smooth outer surfaces. In the late nineteenth century, players observed that the guttie golf balls travelled further as they got older and more gouged up. The players then began to roughen the surface of new golf balls with a hammer to increase flight distance. Manufacturers soon caught on and began molding non-smooth outer surfaces on golf balls.

By the mid 1900's, almost every golf ball being made had 336 dimples arranged in an octahedral pattern. Generally, these balls had about 60% of their outer surface covered by dimples. In 1983, Titleist introduced the TITLEIST 384, which, not surprisingly, had 384 dimples that were arranged in an icosahedral pattern. About 76% of its outer surface was covered with dimples. Today's dimpled golf balls travel nearly two times farther than a similar ball without dimples.

There have also been many patents directed to various dimple patterns. U.S. Pat. No. 4,560,168, which issued to the present inventor, is directed to an icosahedron pattern with six great circles that do not intersect any dimples. The pattern is similar to the present invention in that it has the triangular regions of the icosahedron pattern. However, this type of pattern provided a relatively low surface area coverage, i.e., less than 75% of the outer surface is covered by dimples.

The dimples on a golf ball are important in reducing drag and increasing lift. Drag is the air resistance that acts on the golf ball in the opposite direction from the balls flight direction. As the ball travels through the air, the air surrounding the ball has different velocities and, thus, different pressures. The air exerts maximum pressure at the stagnation point on the front of the ball. The air then flows over the sides of the ball and has increased velocity and reduced pressure. At some point it separates from the surface of the ball, leaving a large turbulent flow area called the wake that has low pressure. The difference in the high pressure in front of the ball and the low pressure behind the ball slows the ball down. This is the primary source of drag for a golf ball.

The dimples on the ball create a turbulent boundary layer around the ball, i.e., the air in a thin layer adjacent to the ball flows in a turbulent manner. The turbulence energizes the boundary layer and helps it stay attached further around the ball to reduce the area of the wake. This greatly increases the pressure behind the ball and substantially reduces the drag.

Lift is the upward force on the ball that is created from a difference in pressure on the top of the ball to the bottom of the ball. The difference in pressure is created by a warpage in the air flow resulting from the ball's back spin. Due to the back spin, the top of the ball moves with the air flow, which delays the separation to a point further aft. Conversely, the bottom of the ball moves against the air flow, moving the

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separation point forward. This asymmetrical separation creates an arch in the flow pattern, requiring the air over the top of the ball to move faster, and thus have lower pressure than the air underneath the ball.

Almost every golf ball manufacturer researches dimple patterns in order to increase the distance travelled by a golf ball. A high degree of dimple coverage is beneficial to flight distance, but only if the dimples are of a reasonable size. Dimple coverage gained by filling spaces with tiny dimples is not very effective, since tiny dimples are not good turbulence generators. Most balls today still have many large spaces between dimples or have filled in these spaces with very small dimples that do not create enough turbulence at average golf ball velocities.

SUMMARY OF THE INVENTION

The present invention is directed to a golf ball dimple pattern that provides a surprisingly better dimple packing than any previous pattern so that a greater percentage of the surface of the golf ball is covered by dimples. The prior art golf balls have dimple patterns that leave many large spaces between adjacent dimples and/or use small dimples to fill in the spaces. The golf balls according to the present invention have triangular regions with a plurality of dimple sizes arranged to provide a remarkably high percentage of dimple coverage while avoiding groupings of relatively large dimples.

The triangular regions have a first set of dimples formed in a large triangle and a second set of dimples formed in a small triangle inside of and adjacent to the large triangle. The first set of dimples forming the large triangle comprises dimples that increase in size from the dimples on the points of the triangle toward the midpoint of the triangle side. Thus, the dimples close to or on the midpoint of the sides of the triangle are the largest dimples on the large triangle. Each dimple diameter along the triangle side is equal to or greater than the adjacent dimple toward the vertex or triangle point. Through this layout and with proper sizing, as set forth below, the dimple coverage is greater than 80% of the surface of the golf ball.

Further, the dimples are arranged so that there are three or less great circle paths that do not intersect any dimples to minimize undimpled surface area. Great circles take up a significant amount of the surface area and an intersection of more than two great circles creates very small angles that have to be filled with very small dimples or large gaps are created.

Still further, the dimples are arranged such that there are no more than two adjacent dimples of the largest diameter. Thus, the largest dimples are more evenly spaced over the ball and are not clumped together.

The golf balls according to the present invention have dimples that cover more than 80% of the outer surface. More importantly, the dimple coverage is not accomplished by the mere addition of very small dimples that do not effectively contribute to the creation of turbulence. Preferably, the total number of dimples is about 300 to about 500 and at least about 80% of the dimples have a diameter of about 0.11 inches or greater. More preferably, at least about 90% of the dimples have a diameter of about 0.11 inches or greater.

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Most preferably, at least about 95% of the dimples have a diameter of about 0.11 inches or greater.

The first embodiment of the present invention is a golf ball having an icosahedron dimple pattern. The pattern comprises 20 triangles made from about 362 dimples and does not have a great circle that does not intersect any dimples. Each of the large triangles, preferably, has an odd number of dimples (7) along each side and the small triangles have an even number of dimples (4) along each side. To properly pack the dimples, the large triangle has nine more dimples than the small triangle. In the first embodiment, the ball has five different sizes of dimples in total. The sides of the large triangle have four different sizes of dimples and the small triangles have two different sizes of dimples.

The second embodiment of the present invention is a golf ball also having an icosahedron dimple pattern. The pattern is substantially similar to the first embodiment, but the large triangle is comprised of three different sizes of dimples and the small triangles have only one size of dimple. In the second embodiment, there are 392 dimples and one great circle that does not intersect any dimples.

The third embodiment of the present invention is a golf ball having an octahedron dimple pattern. The pattern comprises eight triangles made from about 440 dimples and has three great circles that do not intersect any dimples.

In the octahedron pattern, the pattern comprises a third set of dimples formed in a smallest triangle inside of and adjacent to the small triangle. To properly pack the dimples, the large triangle has nine more dimples than the small triangle and the small triangle has nine more dimples than the smallest triangle. In this embodiment, the ball has six different dimple sizes distributed over the surface of the ball. The large triangle has five different dimple sizes, the small triangle has three different dimple sizes and the smallest triangle has two different dimple sizes.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an isometric view of the icosahedron pattern used on the prior art TITLEIST PROFESSIONAL ball showing dimple sizes;

FIG. 2 is an isometric view of the icosahedron pattern used on the prior art TITLEIST PROFESSIONAL ball showing the triangular regions formed by the icosahedron pattern;

FIG. 3 is an isometric view of a first embodiment of a golf ball according to the present invention having an icosahedron pattern, showing dimple sizes;

FIG. 4 is a top view of the golf ball in FIG. 3, showing dimple sizes and arrangement;

FIG. 5 is an isometric view of a second embodiment of a golf ball according to the present invention having an icosahedron pattern, showing dimple sizes and the triangular regions formed from the icosahedron pattern;

FIG. 6 is a top view of the golf ball in FIG. 5, showing dimple sizes and arrangement;

FIG. 7 is a top view of the golf ball in FIG. 5, showing dimple arrangement;

FIG. 8 is a side view of the golf ball in FIG. 5, showing the dimple arrangement at the equator;

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FIG. 9 is a spherical-triangular region of a golf ball according to the present invention having an octahedral dimple pattern, showing dimple sizes; and

FIG. 10 is the spherical triangular region of FIG. 9, showing the triangular dimple arrangement.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIGS. 1 and 2, the TITLEIST PROFESSIONAL golf ball 10 has a plurality of dimples 11 on its outer surface that are formed into a dimple pattern having two sizes of dimples. The first set of dimples A have diameters of about 0.14 inches. The first set of dimples A form the outer triangle 12 of the icosahedron dimple pattern. The second set of dimples B have diameters of about 0.16 inches. The second set of dimples B form the inner triangle 13 and the center dimple 14. The dimples 11 cover less than 80% of the outer surface of the golf ball and there are a significant number of large spaces 15 between adjacent dimples, i.e., spaces that could hold a dimple of 0.03 inches diameter or greater.

Referring now to FIGS. 3 and 4, a golf ball 20 according to the present invention has a plurality of dimples 21 in an icosahedron pattern. In an icosahedron pattern, there are 20 triangular regions that are generally formed from the dimples. The icosahedron pattern has 5 triangles formed at both the top and bottom of the ball. Each of the 5 triangles shares the pole dimple as a point. There are also 10 triangles that extend around the middle of the ball. It is possible to manufacture a golf ball without a great circle equator that does not intersect any dimples. However, most balls have one in order to ease manufacturing and in particular buffing of the golf balls after molding. Also, many players prefer to have an equator so that they can use it to line up putts. Thus, icosahedron patterns generally have modified triangles around the mid-section to create the equator that does not intersect any dimples. The modification to the triangles will be discussed in more detail later with reference to the second embodiment.

In this embodiment, there are five different sized dimples A–E. Dimples B have a greater diameter than dimples A. Dimples C have a greater diameter than dimples B. Dimples D have a greater diameter than dimples C. Dimples E have a greater diameter than dimples D. The preferred dimple sizes are set forth in Table 1 below:

TABLE 1

Dimple	Diameter (inches)
A	.11
B	.14
C	.16
D	.17
E	.18

The dimples are formed in large triangles 22 and small triangles 23. The dimples along the sides of the large triangle 22 increase in diameter toward the midpoint 24 of the sides. The dimple E at the midpoint 24 of the side is the largest dimple along the side and the dimples A at the points 25 of the triangle are the smallest. In this embodiment, each

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dimple along the sides is larger than the adjacent dimple toward the triangle point.

The golf ball **20** has a greater dispersion of the largest dimples. In FIG. **3**, there are four E dimples, the largest diameter, located in the center of the triangles and at the mid-points of the triangle sides. Thus, there are no two adjacent dimples of the largest diameter. This improves dimple packing and aerodynamic uniformity.

Still further, each of the sides of the large triangle **22** has an odd number of dimples and each of the sides of the small triangle **23** has an even number of dimples. The large triangle **22** has nine more dimples than the small triangle **23**. This creates hexagonal packing **26**, i.e., each dimple is surrounded by six other dimples for most of the dimples on the ball. For example, the center E dimple is surrounded by six D dimples. Preferably at least 75% of the dimples have 6 adjacent dimples. More preferably, only the dimples A forming the points of the large triangle **25** do not have hexagonal packing. However, since the dimples A are smaller than the adjacent dimples, the spacing between adjacent dimples is surprisingly small when compared to the prior art golf ball shown in FIG. **1**.

For purposes of this application, adjacent dimples can be considered as any two dimples where the two tangent lines from the first dimple that intersect the center of the second dimple do not intersect any other dimple. Preferably, in the golf balls according to the present invention, less than 30% of the spacings between adjacent dimples is greater than 0.01 inches. More preferably, less than 15% of the spacings between adjacent dimples is greater than 0.01 inches. Thus, the percentage of surface area covered by dimples in the embodiment shown in FIGS. **3** and **4** is about 85.7%, whereas the ball shown in FIG. **1** has less than 80% of its surface covered by dimples. This is very surprising considering that the prior art golf ball was designed for maximum coverage, and even has some dimples which overlap slightly because they are positioned so closely together.

In the golf ball shown in FIG. **3**, there is no great circle path that does not intersect any dimples. This increases the percentage of the outer surface that is covered by dimples, but makes manufacturing more difficult. The golf balls according to the present invention should have the dimples arranged so that there are less than four great circle paths that do not intersect any dimples. In the icosahedron embodiments, there is preferably no great circle path or only one great circle path at the equator that does not intersect any dimples.

In the golf ball shown in FIGS. **3** and **4**, there are 362 dimples. Preferably, the golf balls according to the present invention have about 300 to about 500 dimples in total. More preferably, in the icosahedron type patterns, the golf balls have about 350 to about 450 dimples. Furthermore, the golf balls according to the present invention have a dimple coverage of greater than about 80%. Still further, it is preferred that at least about 80% of the dimples have a diameter of about 0.11 inches or greater so that the majority of the dimples are sufficiently large to assist in creating the turbulent boundary layer. More preferably, the dimples are sized such that at least about 90% of the dimples have a diameter of about 0.11 inches or greater. Most preferably, at least about 95% of the dimples have a diameter of about 0.11 inches or greater.

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Still further, each of the sides of the large triangles is formed from an odd number of dimples. In the icosahedron pattern shown in FIGS. **3** and **4**, there are 7 dimples along each of the sides of the large triangle. Moreover, each side of the small triangle is comprised of sides formed from an even number of dimples. In the icosahedron pattern shown in FIGS. **3** and **4**, there are 4 dimples along each of the sides of the small triangle.

Referring now to FIGS. **5–8**, another golf ball **20** according to the present invention has a plurality of dimples **21** in an icosahedron pattern. In this embodiment, there are again five different sized dimples A–E. Dimples B have a greater diameter than dimples A. Dimples C have a greater diameter than dimples B. Dimples D have a greater diameter than dimples C. Dimples E have a greater diameter than dimples D. The preferred dimple sizes are set forth in Table 2 below:

TABLE 2

Dimple	Diameter (inches)
A	.11
B	.15
C	.155
D	.16
E	.17

In the second embodiment of the present invention shown in FIGS. **5–8**, the dimples are again formed in large triangles **22** and small triangles **23** as shown in FIG. **7**. The dimples along the sides of the large triangle **22** increase in diameter toward the midpoint **24** of the sides. The dimple D at the midpoint **24** of the side is the largest dimple along the side and the dimples A at the points **25** of the triangle are the smallest. In this embodiment, each dimple along the sides is equal to or larger than the adjacent dimple. That is, dimple B is larger than dimple A and dimple D is larger than dimple B.

Like in the first embodiment, each of the sides of the large triangle **22** has a odd number of dimples and each of the sides of the small triangle **23** has an even number of dimples. The large triangle **22** has nine more dimples than the small triangle **23**. This creates the hexagonal packing. Again, the only dimples that do not have hexagonal packing are the points of the triangles, or the A dimples. The percentage of surface area covered by dimples in the second embodiment shown in FIGS. **5–8** is about 82%, whereas the ball shown in FIG. **1** has less than 80% of its surface covered by dimples.

In the golf ball shown in FIGS. **5–8**, there is one great circle path **27** that does not intersect any dimples. This decreases the percentage of the outer surface that is covered by dimples from the first embodiment, but eases manufacturing.

In the golf ball shown in FIGS. **5–8**, there are 392 dimples. All of the dimples have a diameter of about 0.11 inches or greater.

Referring specifically to FIG. **8**, the golf ball in this embodiment has a modified icosahedron pattern to create the great circle path **27** at the equator. The pattern is modified by inserting an extra row of dimples. In the triangular section identified with lettered dimples, there is an extra row **28** of

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D-C-C-D dimples added below the great circle path 27. Thus, the modified icosahedron pattern in the second embodiment has 30 more dimples than the unmodified icosahedron pattern in the first embodiment.

Still further, the golf ball 20 has a greater dispersion of the largest dimples. In FIG. 5, there is only 1 E dimple, the largest diameter, located in the center of the triangles. Thus, there are no two adjacent dimples of the largest diameter. Even the next to the largest dimples D are dispersed at the mid-points of the large triangles such that there are no two adjacent dimples of the two largest diameters, except where extra dimples have been added along the equator. This improves dimple packing and aerodynamic uniformity.

Referring to FIGS. 9 and 10, a golf ball according to the present invention can have an octahedral dimple pattern. In an octahedral dimple pattern, there are 8 spherical triangular regions 30 that form the ball. In this embodiment, there are six different sized dimples A-F. Dimples B have a greater diameter than dimples A. Dimples C have a greater diameter than dimples B. Dimples D have a greater diameter than dimples C. Dimples E have a greater diameter than dimples D. Dimples F have a greater diameter than dimples E. The preferred dimple sizes are set forth in Table 3 below:

TABLE 3

Dimple	Diameter (inches)
A	.09
B	.11
C	.14
D	.15
E	.16
F	.17

In the third embodiment of the present invention shown in FIGS. 9 and 10, the dimples are formed in large triangles 31, small triangles 32 and smallest triangles 33. In this embodiment, each dimple along the sides of the large triangle 31 is equal to or larger than the adjacent dimple from the point 34 to the midpoint 35 of the triangle 31. The dimples E at the midpoint 35 of the side are the largest dimples along the side and the dimples A at the points 34 of the triangle are the smallest. Still further in this embodiment, each dimple along the sides of the small triangle 32 is also equal to or larger than the adjacent dimple from the point 36 to the midpoint 37 of the triangle 32. The dimple F at the midpoint 37 of the side is the largest dimple along the side and the dimples C at the points 36 of the triangle are the smallest.

In this embodiment, each of the sides of the large triangle 31 has an even number of dimples, each of the sides of the small triangle 32 has an odd number of dimples and each of the sides of the smallest triangle 33 has an even number of dimples. The large triangle 31 has nine more dimples than the small triangle 32 and the small triangle 32 has nine more dimples than the smallest triangle 33. This creates the hexagonal packing for all of the dimples inside of the large triangles 31. The percentage of surface area covered by dimples in the third embodiment shown in FIGS. 9 and 10 is about 82%, whereas the prior art octahedral balls have less than 77% of their surface covered by dimples, and most have less than 60%. Thus, there is a significant increase in surface area.

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In the octahedral golf ball shown in FIGS. 9 and 10, there are three great circle paths 38 that do not intersect any dimples. This decreases the percentage of the outer surface that is covered by dimples from the first embodiment, but eases manufacturing.

In the golf ball shown in FIGS. 9 and 10, there are 440 dimples. Preferably, in the octahedral type patterns, the golf balls have about 300 to about 500 dimples. Again, it is preferred that at least about 80% of the dimples have a diameter of about 0.11 inches or greater and, more preferably, that at least about 90% of the dimples have a diameter of about 0.11 inches or greater.

In this embodiment, The sides of the large triangle have an even number of dimples, the sides of the small triangles have an odd number of dimples and the sides of the smallest triangles have an even number of dimples. There are 10 dimples along the sides of the large triangles, 7 dimples along the sides of the small triangles and 4 dimples along the sides of the smallest triangles.

While it is apparent that the illustrative embodiments of the invention herein disclosed fulfill the objectives stated above, it will be appreciated that numerous modifications and other embodiments such as tetrahedrons having four triangles may be devised by those skilled in the art. Therefore, it will be understood that the appended claims are intended to cover all such modifications and embodiments which come within the spirit and scope of the present invention.

What is claimed is:

1. A golf ball having an outside surface with a plurality of round dimples formed thereon having a plurality of dimple diameters, wherein

at least about 80% of the dimples have a diameter of about 0.11 inches or greater and

the dimples cover more than 80% of the outer surface, the dimples comprising a first set of dimples that form a triangle having three point dimples forming points on the triangle and side dimples forming sides of the triangle, wherein all of the side dimples have diameters larger than diameters of the point dimples.

2. The golf ball of claim 1, wherein at least about 90% of the dimples have a diameter of about 0.11 inches or greater.

3. The golf ball of claim 2, wherein at least about 95% of the dimples have a diameter of about 0.11 inches or greater.

4. The golf ball of claim 1, wherein the total number of dimples is between about 300 and about 500.

5. The golf ball of claim 1, wherein at least 75% of the dimples have 6 adjacent dimples.

6. The golf ball of claim 1, wherein the dimples have adjacent dimples and spaces between adjacent dimples and less than 30% of the spaces between adjacent dimples are greater than 0.01 inches.

7. A golf ball having an outside surface with a plurality of round dimples formed thereon having at least three different dimple diameters, wherein at least about 80% of the dimples have a diameter of about 0.11 inches or greater and the dimples cover more than 80% of the outer surface, wherein the total number of dimples is between about 350 and about 450, wherein the dimples have adjacent dimples and spaces between adjacent dimples and less than 30% of the spaces between adjacent dimples are greater than 0.01 inches.

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8. The golf ball of claim 7, wherein at least about 90% of the dimples have a diameter of about 0.11 inches or greater.

9. The golf ball of claim 8, wherein at least about 95% of the dimples have a diameter of about 0.11 inches or greater.

10. The golf ball of claim 7, wherein at least 75% of the dimples have 6 adjacent dimples.

11. The golf ball of claim 7, wherein no two dimples overlap.

12. The golf ball of claim 7, further including at least four different dimple diameters.

13. The golf ball of claim 7, wherein the dimples cover more than 85% of the outer surface.

14. The golf ball of claim 7, wherein the dimples form a plurality of spherical-triangular regions, wherein each region has a set of dimples formed in a large triangle having three sides and three points, the first dimples at the points having a first diameter, the second dimples at the mid-point of each of the sides having a second diameter, and at least one third dimple between each second and first dimple having a third diameter, and the second diameter is greater

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than the first and third diameters, the golf ball further includes a center dimple within the large triangle having a fourth diameter equal to the second diameter.

15. The golf ball of claim 14, wherein the second dimples and the center dimple are not adjacent one another.

16. The golf ball of claim 7, wherein the dimples form a plurality of spherical-triangular regions, wherein each region has a set of dimples formed in a large triangle having three sides and three points, each of the dimples at the points is surrounded by less than six other dimples.

17. The golf ball of claim 7, said dimples being arranged so that there are less than four great circle paths that do not intersect any dimples.

18. The golf ball of claim 7, said dimples being arranged so that there is only one great circle path at the equator of the ball that does not intersect any dimples.

19. The golf ball of claim 7, further including at least five different dimple diameters.

* * * * *

Exhibit H

US007163472B2

(12) **United States Patent**
Dalton et al.(10) **Patent No.:** **US 7,163,472 B2**
(45) **Date of Patent:** ***Jan. 16, 2007**(54) **GOLF BALL DIMPLES WITH A CATENARY CURVE PROFILE**(75) Inventors: **Jeffrey L. Dalton**, Dartmouth, MA (US); **Laurent Bissonnette**, Portsmouth, RI (US)(73) Assignee: **Acushnet Company**, Fairhaven, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **10/827,643**(22) Filed: **Apr. 20, 2004**(65) **Prior Publication Data**

US 2004/0198537 A1 Oct. 7, 2004

Related U.S. Application Data

(63) Continuation of application No. 09/989,191, filed on Nov. 21, 2001, now Pat. No. 6,796,912.

(51) **Int. Cl.**
A63B 37/12 (2006.01)(52) **U.S. Cl.** **473/383**(58) **Field of Classification Search** 473/378-385
See application file for complete search history.(56) **References Cited****U.S. PATENT DOCUMENTS**

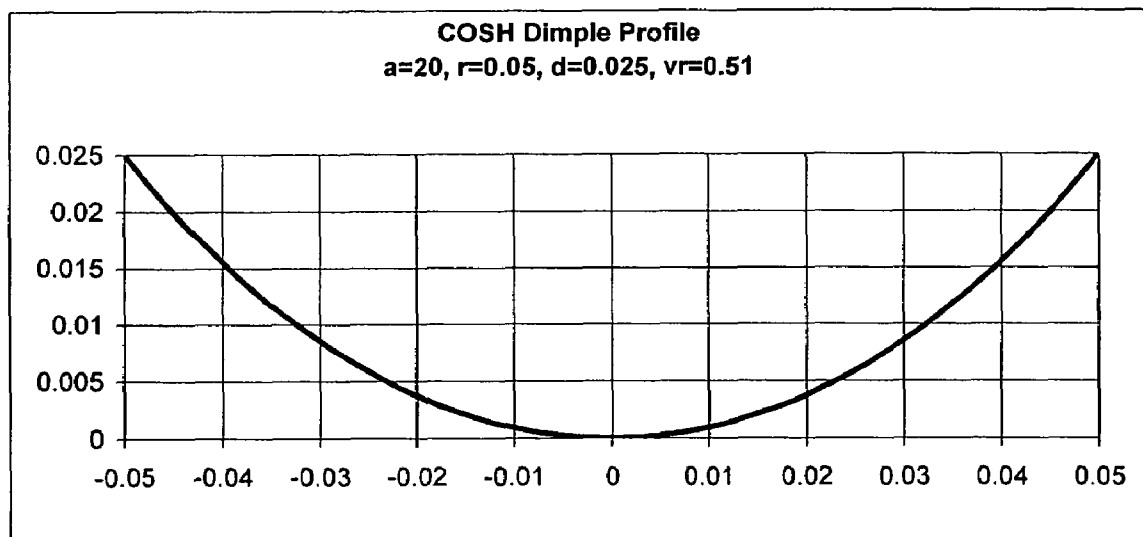
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Primary Examiner—Raeann Gorden(74) *Attorney, Agent, or Firm*—Bingham McCutchen LLP(57) **ABSTRACT**

A golf ball having an outside surface with a plurality of dimples formed thereon. The dimples on the ball have a cross-sectional profiles formed by a catenary curve. Shape constants in the catenary curve are used to vary the ball flight performance according to ball spin characteristics and player swing speed.

21 Claims, 4 Drawing Sheets

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FIG. 1

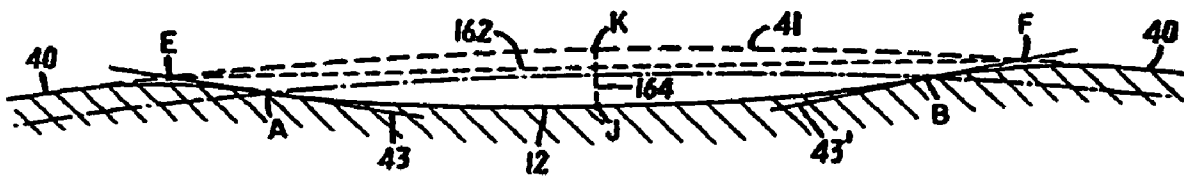


FIG. 2

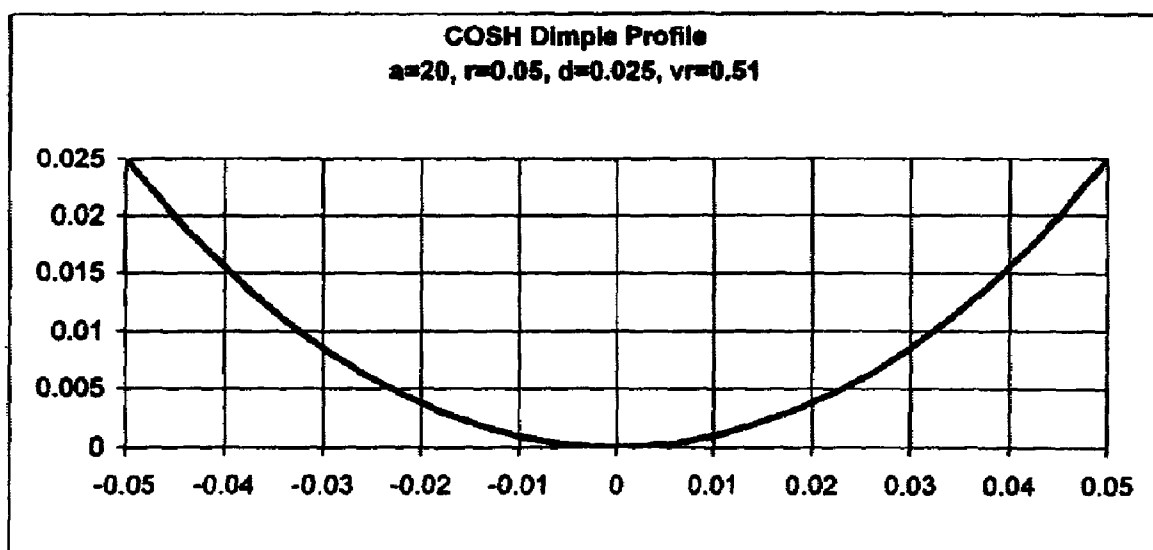


FIG. 3

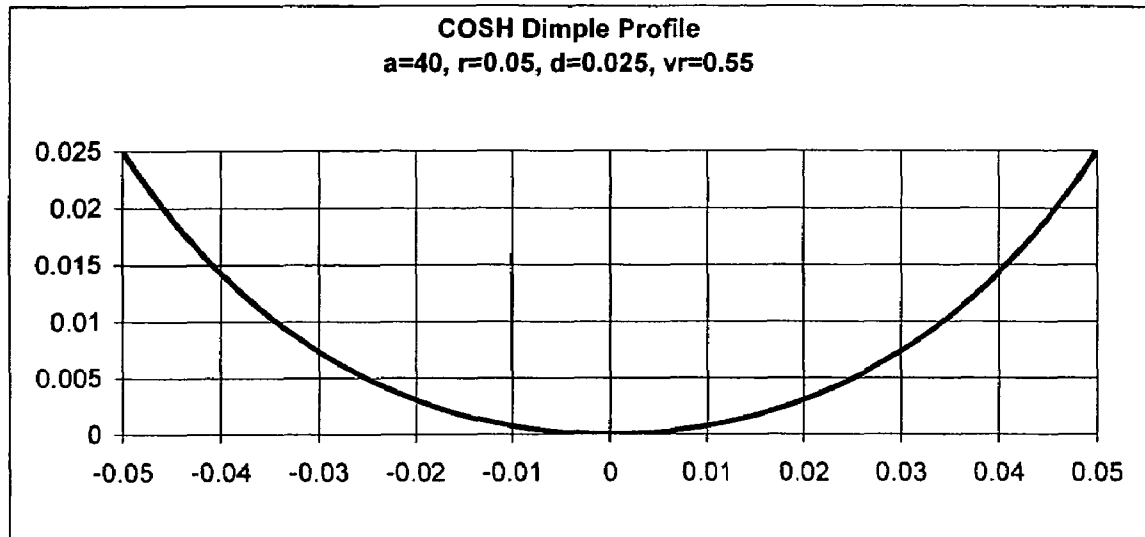


FIG. 4

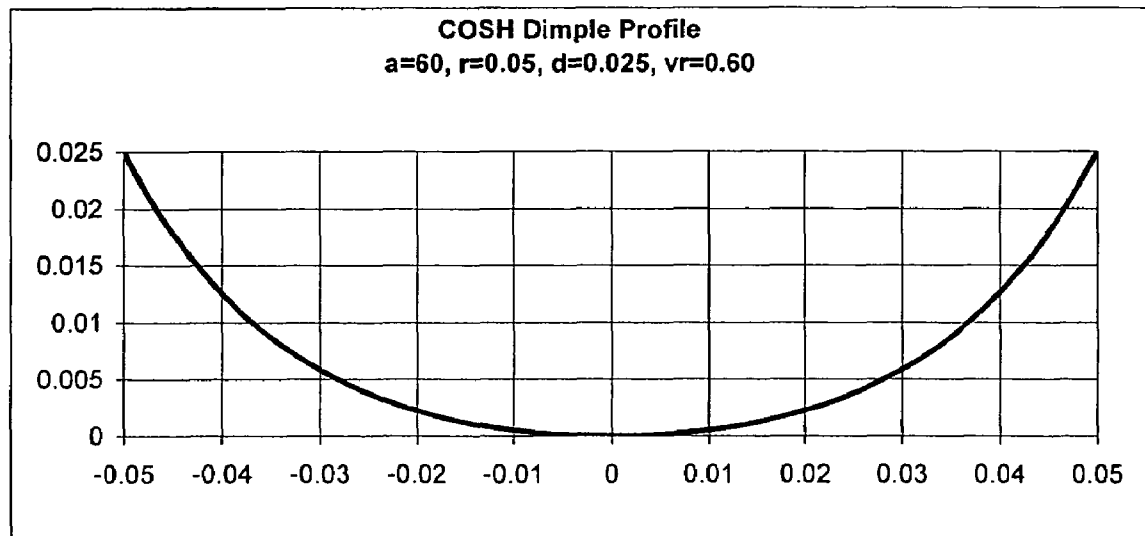


FIG. 5

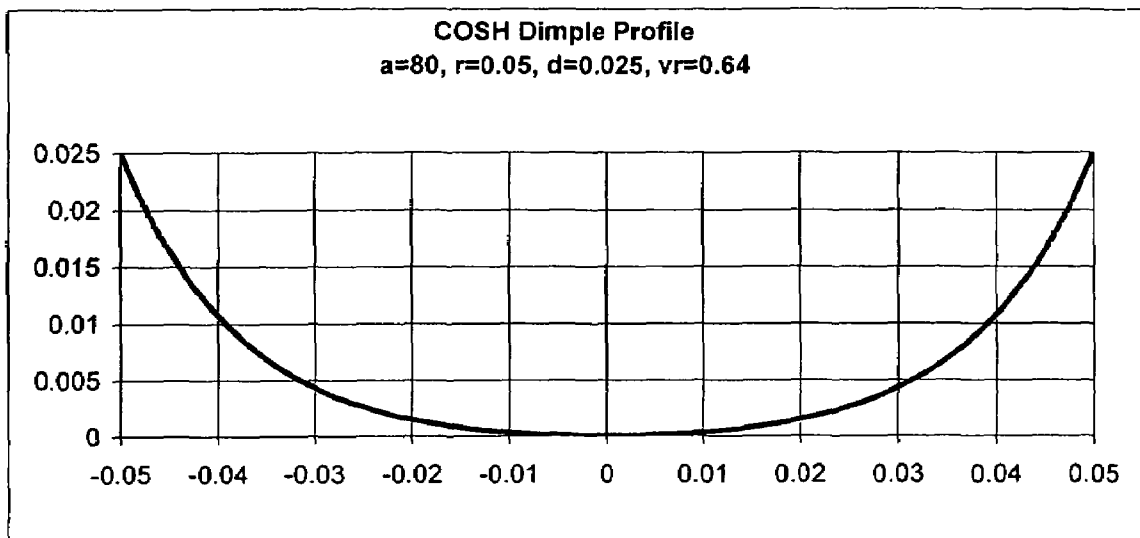
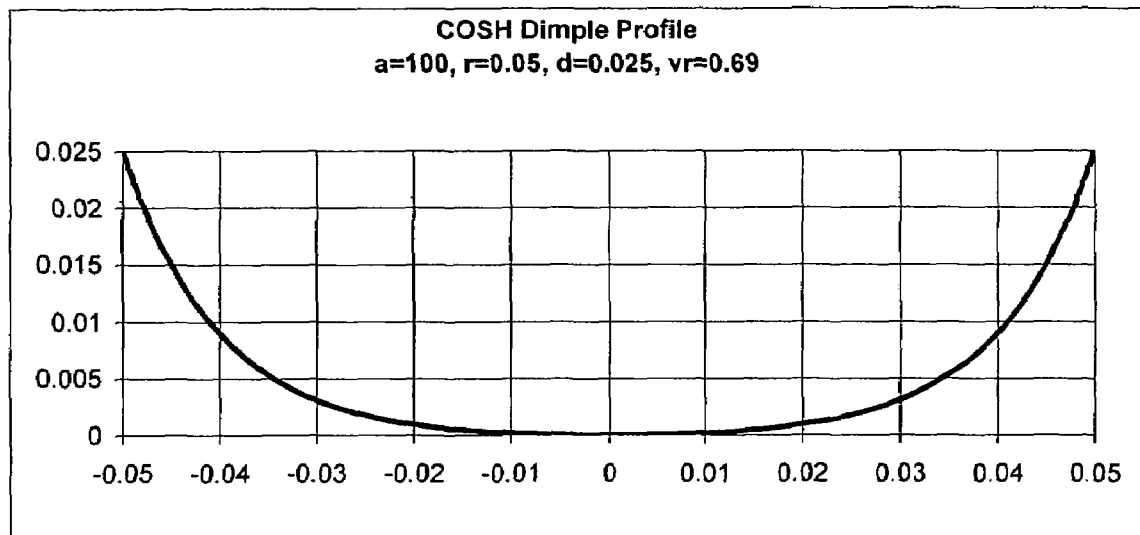


FIG. 6



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GOLF BALL DIMPLES WITH A CATENARY CURVE PROFILE**CROSS REFERENCE TO RELATED APPLICATIONS**

This application is a continuation of U.S. application Ser. No. 09/989,191, filed Nov. 21, 2001, the entirety of which is incorporated by reference herein.

FIELD OF INVENTION

The present invention relates to a golf ball, and more particularly, to the cross sectional profile of dimples on the surface of a golf ball.

BACKGROUND OF THE INVENTION

Golf balls were originally made with smooth outer surfaces. In the late nineteenth century, players observed that the guttie golf balls traveled further as they got older and more gouged up. The players then began to roughen the surface of new golf balls with a hammer to increase flight distance. Manufacturers soon caught on and began molding non-smooth outer surfaces on golf balls.

By the mid 1900's, almost every golf ball being made had 336 dimples arranged in an octahedral pattern. Generally, these balls had about 60 percent of their outer surface covered by dimples. Over time, improvements in ball performance were developed by utilizing different dimple patterns. In 1983, for instance, Titleist introduced the TITLEIST 384, which, not surprisingly, had 384 dimples that were arranged in an icosahedral pattern. About 76 percent of its outer surface was covered with dimples. Today's dimpled golf balls travel nearly two times farther than a similar ball without dimples.

The dimples on a golf ball are important in reducing drag and increasing lift. Drag is the air resistance that acts on the golf ball in the opposite direction from the ball flight direction. As the ball travels through the air, the air surrounding the ball has different velocities and, thus, different pressures. The air exerts maximum pressure at the stagnation point on the front of the ball. The air then flows over the sides of the ball and has increased velocity and reduced pressure. At some point it separates from the surface of the ball, leaving a large turbulent flow area called the wake that has low pressure. The difference in the high pressure in front of the ball and the low pressure behind the ball slows the ball down. This is the primary source of drag for a golf ball.

The dimples on the ball create a turbulent boundary layer around the ball, i.e., the air in a thin layer adjacent to the ball flows in a turbulent manner. The turbulence energizes the boundary layer and helps it stay attached further around the ball to reduce the area of the wake. This greatly increases the pressure behind the ball and substantially reduces the drag.

Lift is the upward force on the ball that is created from a difference in pressure on the top of the ball to the bottom of the ball. The difference in pressure is created by a warpage in the air flow resulting from the ball's back spin. Due to the back spin, the top of the ball moves with the air flow, which delays the separation to a point further aft. Conversely, the bottom of the ball moves against the air flow, moving the separation point forward. This asymmetrical separation creates an arch in the flow pattern, requiring the air over the top of the ball to move faster, and thus have lower pressure than the air underneath the ball.

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Almost every golf ball manufacturer researches dimple patterns in order to increase the distance traveled by a golf ball. A high degree of dimple coverage is beneficial to flight distance, but only if the dimples are of a reasonable size. Dimple coverage gained by filling spaces with tiny dimples is not very effective, since tiny dimples are not good turbulence generators.

In addition to researching dimple pattern and size, golf ball manufacturers also study the effect of dimple shape, volume, and cross-section on overall flight performance of the ball. One example is U.S. Pat. No. 5,737,757, which discusses making dimples using two different spherical radii with an inflection point where the two curves meet. In most cases, however, the cross-sectional profiles of dimples in prior art golf balls are parabolic curves, ellipses, semi-spherical curves, saucer-shaped, a sine curve, a truncated cone, or a flattened trapezoid. One disadvantage of these shapes is that they can sharply intrude into the surface of the ball, which may cause the drag to become greater than the lift. As a result, the ball may not make best use of momentum initially imparted thereto, resulting in an insufficient carry of the ball. Despite all the cross-sectional profiles disclosed in the prior art, there has been no disclosure of a golf ball having dimples defined by the revolution of a catenary curve.

SUMMARY OF THE INVENTION

The present invention is directed to defining dimples on a golf ball by revolving a catenary curve about its symmetrical axis. In one embodiment, the catenary curve is defined by a hyperbolic sine function. In another embodiment, the catenary curve is defined by a hyperbolic cosine function. In a preferred embodiment, the catenary curve used to define a golf ball dimple is a hyperbolic cosine function in the form of:

$$Y=d(\cos(ax)-1)/\cos h(ar)-1$$

where: Y is the vertical distance from the dimple apex, x is the radial distance from the dimple apex, a is the shape constant; d is the depth of the dimple, and r is the radius of the dimple.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other aspects of the present invention may be more fully understood with reference to, but not limited by, the following drawings.

FIG. 1 shows a method for measuring the depth and radius of a dimple;

FIG. 2 is a dimple cross-sectional profile defined by a hyperbolic cosine function, cosh, with a shape constant of 20, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.51;

FIG. 3 is a dimple cross-sectional profile defined by a hyperbolic cosine function, cosh, with a shape constant of 40, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.55;

FIG. 4 is a dimple cross-sectional profile defined by a hyperbolic cosine function, cosh, with a shape constant of 60, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.60;

FIG. 5 is a dimple cross-sectional profile defined by a hyperbolic cosine function, cosh, with a shape constant of

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80, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.64; and

FIG. 6 is a dimple cross-sectional profile defined by a hyperbolic cosine function, cosh, with a shape constant of 100, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.69.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is a golf ball which comprises dimples defined by the revolution of a catenary curve about an axis. A catenary curve represents the curve formed by a perfectly flexible, uniformly dense, and inextensible cable suspended from its endpoints. In general, the mathematical formula representing such a curve is expressed as the equation:

$$y = a \cosh(bx)$$

where a and b are constants, y is the vertical axis and x is the horizontal axis on a two dimensional graph. The dimple shape on the golf ball is generated by revolving the catenary curve about its y axis.

The present invention uses variations of this mathematical expression to define the cross-section of golf ball dimples. In the present invention, the catenary curve is defined by hyperbolic sine or cosine functions. A hyperbolic sine function is expressed as follows:

$$\sinh(x) = \frac{e^x - e^{-x}}{2}$$

while a hyperbolic cosine function is expressed by the following formula:

$$\cosh(x) = \frac{e^x + e^{-x}}{2}$$

In one embodiment of the present invention, the mathematical equation for describing the cross-sectional profile of a dimple is expressed by the following formula:

$$Y = \frac{d(\cosh(ax) - 1)}{\cosh(ar) - 1}$$

where: Y is the vertical distance from the dimple apex;

x is the radial distance from the dimple apex to the dimple surface;

a is a shape constant (also called shape factor);

d is the depth of the dimple; and

r is the radius of the dimple.

The "shape constant" or "shape factor", a, is an independent variable in the mathematical expression for a catenary curve. The shape factor may be used to independently alter the volume ratio of the dimple while holding the dimple depth and radius fixed. The volume ratio is the fractional ratio of the dimple volume divided by the volume of a cylinder defined by a similar radius and depth as the dimple.

Use of the shape factor provides an expedient method of generating alternative dimple profiles, for dimples with fixed radii and depth. For example, if a golf ball designer desires

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to generate balls with alternative lift and drag characteristics for a particular dimple position, radius, and depth on a golf ball surface, then the golf ball designer may simply describe alternative shape factors to obtain alternative lift and drag performance without having to change these other parameters. No modification to the dimple layout on the surface of the ball is required.

The depth (d) and radius (r) (r=1/2 diameter (D)) of the dimple may be measured as described in U.S. Pat. No. 4,729,861 (shown in FIG. 1), the disclosure of which is incorporated by reference in its entirety.

For the equation provided above, shape constant values that are larger than 1 result in dimple volume ratios greater than 0.5. Preferably, shape factors are between about 20 to about 100. FIGS. 2-6 illustrate dimple profiles for shape factors of 20, 40, 60, 80, and 100, respectively. Table 1 illustrates how the volume ratio changes for a dimple with a radius of 0.05 inches and a depth of 0.025 inches.

TABLE 1

Shape Factor	Volume Ratio
20	0.51
40	0.55
60	0.60
80	0.64
100	0.69

As shown above, increases in shape factor result in higher volume ratios for a given dimple radius and depth.

A dimple whose profile is defined by the cosh catenary curve with a shape constant of less than about 40 will have a smaller dimple volume than a dimple with a spherical profile. This will result in a higher trajectory and longer carry distance. On the other hand, a dimple whose profile is defined by the cosh catenary curve with a shape constant of greater than about 40 will have a larger dimple volume than a dimple with a spherical profile. This will result in a lower trajectory and longer total distance.

Therefore, a golf ball having dimples defined by a catenary curve with a shape constant is advantageous because the shape constant may be selected to optimize the flight profile of specific ball designs. For example, one would preferably select a shape factor greater than about 40, more preferably greater than about 50, for balls which exhibit high spin rate characteristics. Conversely, one would select a low shape factor for balls which exhibit low spin rate characteristics. For instance a designer may select a shape factor lower than about 50, or more preferably less than about 40, for low spin balls. Thus, golf balls with dimples described by the revolution of a catenary curve allow for improved ball performance and more efficient variability of design. Furthermore, the shape factor of catenary curves provides golf ball designers with a simple single factor for trajectory optimization.

In addition to designing a dimple shape according to the ball spin characteristics, the use of a catenary curve profile allows designers to more easily consider the player swing speed in optimizing ball performance. The flight distance and roll of a golf ball are strongly influenced by the ball speed, launch angle and spin rate obtained as a result of collision with the club. The lift and drag generated during the ball's flight are influenced by atmospheric conditions, ball size, and dimple geometry. To obtain maximum distance the dimple geometry may be selected such that an optimal combination of lift and drag is obtained. The dimple shape

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factor may thus be used to provide balls that yield optimal flight performance for specific swing speed categories. The advantageous feature of shape factor is that dimple location need not be manipulated for each swing speed; only the dimple shape will be altered. Thus, a “family” of golf balls may have a similar general appearance although the dimple shape is altered to optimize flight characteristics for particular swing speeds. Table 2 identifies examples of preferred ball designs for players of differing swing speeds.

TABLE 2

Ball Design	Dimple Shape Factor	Ball Speed from driver (mph)	Cover Hardness (Shore D)	Ball Compression (Atti)
1	80	155–175	45–55	60–75
2	90	155–175	45–55	75–90
3	100	155–175	45–55	90–105
4	70	155–175	55–65	60–75
5	80	155–175	55–65	75–90
6	90	155–175	55–65	90–105
7	55	155–175	65–75	60–75
8	65	155–175	65–75	75–90
9	75	155–175	65–75	90–105
10	65	140–155	45–55	60–75
11	75	140–155	45–55	75–90
12	85	140–155	45–55	90–105
13	55	140–155	55–65	60–75
14	65	140–155	55–65	75–90
15	75	140–155	55–65	90–105
16	40	140–155	65–75	60–75
17	50	140–155	65–75	75–90
18	60	140–155	65–75	90–105
19	50	125–140	45–55	60–75
20	60	125–140	45–55	75–90
21	70	125–140	45–55	90–105
22	40	125–140	55–65	60–75
23	50	125–140	55–65	75–90
24	60	125–140	55–65	90–105
25	25	125–140	65–75	60–75
26	35	125–140	65–75	75–90
27	45	125–140	65–75	90–105

Table 2 shows that as the spin rate and ball speed increase the shape factor should also increase to provide optimal aerodynamic performance, increased flight distance. While the shape factors listed above illustrate preferred embodiments for varying ball constructions and ball speeds, the shape factors listed above for each example may be varied without departing from the spirit and scope of the present invention. For instance, in one embodiment the shape factors listed for each example above may be adjusted upwards or downwards by 20 to arrive at a further customized ball design. More preferably, the shape factors may be adjusted upwards or downwards by 10, and even more preferably it may be adjusted by 5.

To illustrate the selection of shape factors in dimple design from Table 2, the preferred dimple shape factor for a ball having a cover hardness of about 45 to about 55 Shore D and a ball compression of about 60 to about 75 Atti for a player with a ball speed from the driver between about 140 and about 155 mph would be about 65. Likewise, the preferred shape factor for the same ball construction, but for a player having a ball speed from the driver of between about 155 mph and about 175 mph would be about 80. As mentioned above, these preferred shape factors may be adjusted upwards or downwards by 20, 10, or 5 to arrive at a further customized ball design.

Thus, shape factors may be selected for a particular ball construction that result in a ball designed to work well with a wide variety of player swing speeds. For instance, in one embodiment of the present invention, a shape factor between

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about 65 and about 100 would be suitable for a ball with a cover hardness between about 45 and about 55 shore D.

The present invention may be used with practically any type of ball construction. For instance, the ball may have a 2-piece design, a double cover or veneer cover construction depending on the type of performance desired of the ball. Examples of these and other types of ball constructions that may be used with the present invention include those described in U.S. Pat. Nos. 5,713,801, 5,803,831, 5,885,172, 5,919,100, 5,965,669, 5,981,654, 5,981,658, and 6,149,535, as well as in Publication No. US2001/0009310 A1. Different materials also may be used in the construction of the golf balls made with the present invention. For example, the cover of the ball may be made of polyurethane, ionomer resin, balata or any other suitable cover material known to those skilled in the art. Different materials also may be used for forming core and intermediate layers of the ball. After selecting the desired ball construction, the flight performance of the golf ball can be adjusted according to the design, placement, and number of dimples on the ball. As explained above, the use of catenary curves provides a relatively effective way to modify the ball flight performance without significantly altering the dimple pattern. Thus, the use of catenary curves defined by shape factors allows a golf ball designer to select flight characteristics of a golf ball in a similar way that different materials and ball constructions can be selected to achieve a desired performance.

While the present invention is directed toward using a catenary curve for at least one dimple on a golf ball, it is not necessary that catenary curves be used on every dimple on a golf ball. In some cases, the use of a catenary curve may only be used for a small number of dimples. It is preferred, however, that a sufficient number of dimples on the ball have catenary curves so that variation of shape factors will allow a designer to alter the ball's flight characteristics. Thus, it is preferred that a golf ball have at least about 30%, and more preferably at least about 60%, of its dimples defined by a catenary curves.

Moreover, it is not necessary that every dimple have the same shape factor. Instead, differing combinations of shape factors for different dimples on the ball may be used to achieve desired ball flight performance. For example, some of the dimples defined by catenary curves on a golf ball may have one shape factor while others have a different shape factor. In addition, the use of differing shape factors may be used for different diameter dimples. While two or more shape factors may be used for dimples on a golf ball, it is preferred that the differences between the shape factors be relatively similar in order to achieve optimum ball flight performance that corresponds to a particular ball construction and player swing speed. Preferably, a plurality of shape factors used to define dimples having catenary curves do not differ by more than 30, and even more preferably have shape factors that do not differ by more than 15.

Desirable dimple characteristics are more precisely defined by aerodynamic lift and drag coefficients, C_l and C_d respectively. These aerodynamic coefficients are used to quantify the force imparted to a ball in flight. The lift and drag forces are computed as follows:

$$F_{lift}=0.5\rho C_l A V^2$$

$$F_{drag}=0.5\rho C_d A V^2$$

where: ρ =air density

C_l =lift coefficient

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 C_d =drag coefficientA=ball area= πr^2 (where r =ball radius), and

V=ball velocity

Lift and drag coefficients are dependent on air density, air viscosity, ball speed, and spin rate. A common dimensionless quantity for tabulating lift and drag coefficients is Reynolds number. Reynolds number quantifies the ratio of inertial to viscous forces acting on an object moving in a fluid. Reynolds number is calculated as follows:

$$R = \frac{VD\rho}{\mu}$$

where: R=Reynolds number

V=velocity

D=ball diameter

 ρ =air density, and μ =air viscosity

In the examples that follow, standard atmospheric values of 0.00238 slug/ft³ for air density and 3.74×10⁻⁷ lb*sec/ft² for air viscosity are used to calculate Reynolds number. For example, at standard atmospheric conditions a golf ball with a velocity of 160 mph would have a Reynolds number of 209,000. typically, the lift and drag coefficients of a golf ball are measured at a variety of spin rates and Reynolds numbers. For example, U.S. Pat. No. 6,186,002 teaches the use of a series of ballistic screens to acquire lift and drag coefficients at numerous spin rates and Reynolds numbers. Other techniques utilized to measure lift and drag coefficients include conventional wind tunnel tests. One skilled in the art of aerodynamics testing could readily determine the lift and drag coefficients with either wind tunnel or ballistic screen technology. An additional parameter often used to characterize the air flow over rotating bodies is the spin ratio. Spin ratio is the rotational surface speed of the body divided by the free stream velocity. The spin ratio is calculated as follows:

$$SpinRatio = \frac{2(rps)\pi r}{V}$$

where: rps=revolutions per second of the ball

r=ball radius, and

V=ball velocity

For a golf ball of any diameter and weight, increased distance is obtained when the lift force, F_{lift} , on the ball is greater than the weight of the ball but preferably less than three times its weight. This may be expressed as:

$$W_{ball} \leq F_{lift} \leq 3W_{ball}$$

The preferred lift coefficient range which ensures maximum flight distance is thus:

$$\frac{2W_{ball}}{\pi r^2 V^2} \leq C_l \leq \frac{6W_{ball}}{\pi r^2 V^2}$$

The lift coefficients required to increase flight distance for golfers with different ball launch speeds may be computed using the formula provided above. Table 3 provides several examples of the preferred range for lift coefficients for alternative launch speeds, ball size, and weight:

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TABLE 3

PREFERRED RANGES FOR LIFT COEFFICIENT FOR A GIVEN BALL DIAMETER, WEIGHT, AND LAUNCH VELOCITY FOR A GOLF BALL ROTATING AT 3000 RPM

	Preferred Minimum C_l	Preferred Maximum C_l	Ball Diameter (in.)	Ball Weight (oz.)	Ball Velocity (ft/s)	Reynolds Number	Spin Ratio
10	0.09	0.27	1.75	1.8	250	232008	0.092
	0.08	0.24	1.75	1.62	250	232008	0.092
	0.07	0.21	1.75	1.4	250	232008	0.092
	0.10	0.29	1.68	1.8	250	222727	0.088
	0.09	0.27	1.68	1.62	250	222727	0.088
15	0.08	0.23	1.68	1.4	250	222727	0.088
	0.12	0.37	1.5	1.8	250	198864	0.079
	0.11	0.33	1.5	1.62	250	198864	0.079
	0.10	0.29	1.5	1.4	250	198864	0.079
	0.14	0.42	1.75	1.8	200	185606	0.115
	0.13	0.38	1.75	1.62	200	185606	0.115
20	0.11	0.33	1.75	1.4	200	185606	0.115
	0.15	0.46	1.68	1.8	200	178182	0.110
	0.14	0.41	1.68	1.62	200	178182	0.110
	0.12	0.36	1.68	1.4	200	178182	0.110
	0.19	0.58	1.5	1.8	200	159091	0.098
	0.17	0.52	1.5	1.62	200	159091	0.098
25	0.15	0.45	1.5	1.4	200	159091	0.098

Once a dimple pattern is selected for the golf ball a shape factor for a catenary dimple profile may be used to achieve the desired lift coefficient. Dimple patterns that provide a high percentage of surface coverage are preferred, and are well known in the art. For example, U.S. Pat. Nos. 5,562, 552, 5,575,477, 5,957,787, 5,249,804, and 4,925,193 disclose geometric patterns for positioning dimples on a golf ball. In one embodiment of the present invention, the dimple pattern is at least partially defined by phyllotaxis-based patterns, such as those described in copending U.S. patent application Ser. No. 09/418,003, which is incorporated by reference in its entirety. Preferably a dimple pattern that provides greater than about 50% surface coverage is selected. Even more preferably, the dimple pattern provides greater than about 70% surface coverage. Once the dimple pattern is selected, several alternative shape factors for the catenary profile can be tested in a wind tunnel or light gate test range to empirically determine the catenary shape factor that provides the desired lift coefficient at the desired launch velocity. Preferably, the measurement of lift coefficient is performed with the golf ball rotating at typical driver rotation speeds. A preferred spin rate for performing the lift and drag tests is 3,000 rpm.

The catenary shape factor may thus be used to provide a family of golf balls which have the same dimple pattern but alternative catenary shape factors. The catenary shape factors allow the ball designer to tailor each ball in the family for maximum distance for a given launch speed. Furthermore, the golf balls may be of a variety of alternative sizes and weights.

As discussed above, catenary curves may be used to define dimples on any type of golf ball, including golf balls having solid, wound, liquid filled or dual cores, or golf balls having multilayer intermediate layer or cover layer constructions. While different ball construction may be selected for different types of playing conditions, the use of catenary curves would allow greater flexibility to ball designers to better customize a golf ball to suit a player.

While the invention has been described in conjunction with specific embodiments, it is evident that numerous

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alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description.

What is claimed is:

1. A golf ball having a plurality of recessed dimples on the surface thereof, wherein at least one dimple is defined by the revolution of a Catenary curve, and wherein the ball has a cover hardness of about 45 to about 55 Shore D, a compression of about 60 to 75 Atti, and a shape factor of about 65.

2. The golf ball of claim 1, wherein the golf ball has lift coefficient from 0.09 to 0.27 at a Reynolds Number of 222727 and a Spin Ratio of 0.088.

3. The golf ball of claim 1, wherein the golf ball has lift coefficient from 0.14 to 0.41 at a Reynolds Number of 178182 and a Spin Ratio of 0.110.

4. The golf ball of claim 1, of the plurality of recessed dimples are defined by the revolution of a Catenary curve.

5. A golf ball having a core and a cover, wherein the cover has a plurality of recessed dimples on the surface thereof, wherein at least one dimple is defined by the revolution of a Catenary curve, and wherein the golf ball has a lift coefficient from 0.09 to 0.27 at a Reynolds Number of 222727 to 0.088.

6. The golf ball of claim 5, wherein the shape factor is from 80 to 100 and the cover has a hardness of 45 to 55 Shore D.

7. The golf ball of claim 5, wherein the shape factor is from 70 to 90 and the cover has a hardness of 55 to 65 Shore D.

8. The golf ball of claim 5, wherein the shape factor is from 50 to 70 and the cover has a hardness of 45 to 55 Shore D.

9. The golf ball of claim 5, wherein the shape factor is from 40 to 60 and the cover has a hardness of 55 to 65 Shore D.

10. The golf ball of claim 5, wherein the shape factor is from 25 to 45 and the cover has a hardness of 65 to 75 Shore D.

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11. The golf ball of claim 5, wherein about 30 percent or greater of the plurality of recessed dimples are defined by the revolution of a Catenary curve.

12. A golf ball having a core and a cover, wherein the cover has a plurality of recessed dimples on the surface thereof, wherein at least one dimple is defined by the revolution of a Catenary curve, and wherein the golf ball has a lift coefficient from 0.14 to 0.41 at a Reynolds Number of 178182 to 0.110.

13. The golf ball of claim 12, wherein the shape factor is from 80 to 100 and the cover has a hardness of 45 to 55.

14. The golf ball of claim 12, wherein the shape factor is from 70 to 90 and the cover has a hardness of 55 to 65.

15. The golf ball of claim 12, wherein the shape factor is from 50 to 70 and the cover has a hardness of 45 to 55.

16. The golf ball of claim 12, wherein the shape factor is from 40 to 60 and the cover has a hardness of 55 to 65.

17. The golf ball of claim 12, wherein the shape factor is from 25 to 45 and the cover has a hardness of 65 to 75.

18. The golf ball of claim 12, wherein about 30 percent or greater of the plurality of recessed dimples are defined by the revolution of a Catenary curve.

19. A golf ball having a plurality of recessed dimples on the surface thereof, wherein at least one dimple is defined by the revolution of a Catenary curve, and wherein the ball has a cover hardness of about 45 to about 55 Shore D, a compression of about 60 to 75 Atti, and a shape factor of about 80.

20. The golf ball of claim 19, wherein the golf ball has a lift coefficient from 0.09 to 0.27 at a Reynolds Number of 222727 and a Spin Ratio of 0.088 or a lift coefficient from 0.14 to 0.41 at a Reynolds Number of 178182 and a Spin Ratio of 0.110.

21. The golf ball of claim 1, wherein the golf ball has a ball speed from a driver of 140 mph to 155 mph.

* * * * *

Exhibit I

(12) **United States Patent**
Aoyama et al.

(10) **Patent No.:** **US 7,887,439 B2**
(45) **Date of Patent:** ***Feb. 15, 2011**

(54) **GOLF BALL DIMPLES WITH A CATENARY CURVE PROFILE**

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Nicholas M. Nardacci, Fairhaven, MA (US)

(73) Assignee: **Acushnet Company**, Fairhaven, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **12/632,909**

(22) Filed: **Dec. 8, 2009**

(65) **Prior Publication Data**

US 2010/0081519 A1 Apr. 1, 2010

Related U.S. Application Data

(60) Continuation of application No. 12/071,087, filed on Feb. 15, 2008, now Pat. No. 7,641,572, which is a continuation-in-part of application No. 11/907,195, filed on Oct. 10, 2007, now Pat. No. 7,491,137, which is a continuation of application No. 11/607,916, filed on Dec. 4, 2006, now abandoned, which is a continuation of application No. 11/108,812, filed on Apr. 19, 2005, now Pat. No. 7,156,757, which is a continuation of application No. 10/784,744, filed on Feb. 24, 2004, now Pat. No. 6,913,550, which is a continuation of application No. 10/096,852, filed on Mar. 14, 2002, now Pat. No. 6,729,976, which is a continuation-in-part of application No. 09/989,191, filed on Nov. 21, 2001, now Pat. No. 6,796,912, and a continuation-in-part of application No. 09/404,164, filed on Sep. 27, 1999, now Pat. No. 6,358,161, which is a division of application No. 08/922,633, filed on Sep. 3, 1997, now Pat. No. 5,957,786.

(51) **Int. Cl.**
A63B 37/12 (2006.01)

(52) **U.S. Cl.** **473/383**

(58) **Field of Classification Search** 473/383-385
See application file for complete search history.

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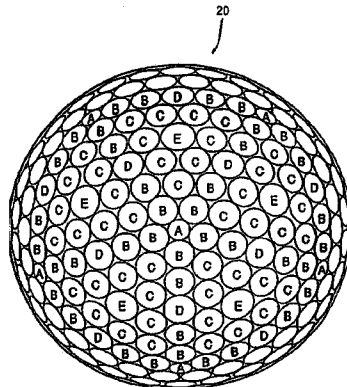
Primary Examiner—Raeann Trimiew

(74) *Attorney, Agent, or Firm*—Murphy & King, P.C.

(57) **ABSTRACT**

A golf ball having an outside surface with a plurality of dimples formed thereon. The dimples on the ball have a cross-sectional profiles formed by a catenary curve. Combinations of varying dimple diameters, shape factors, and chordal depths in the catenary curve are used to vary the ball flight performance according to ball spin characteristics, player swing speed, as well as satisfy specific aerodynamic magnitude and direction criteria.

20 Claims, 22 Drawing Sheets



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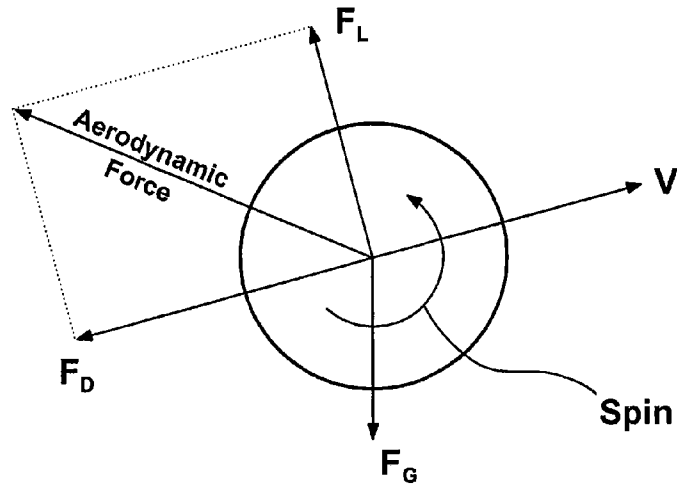


FIG. 1

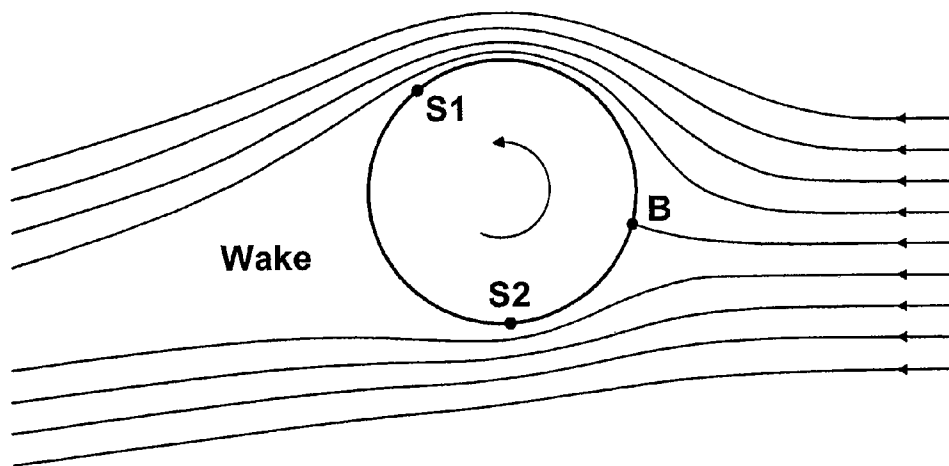


FIG. 2

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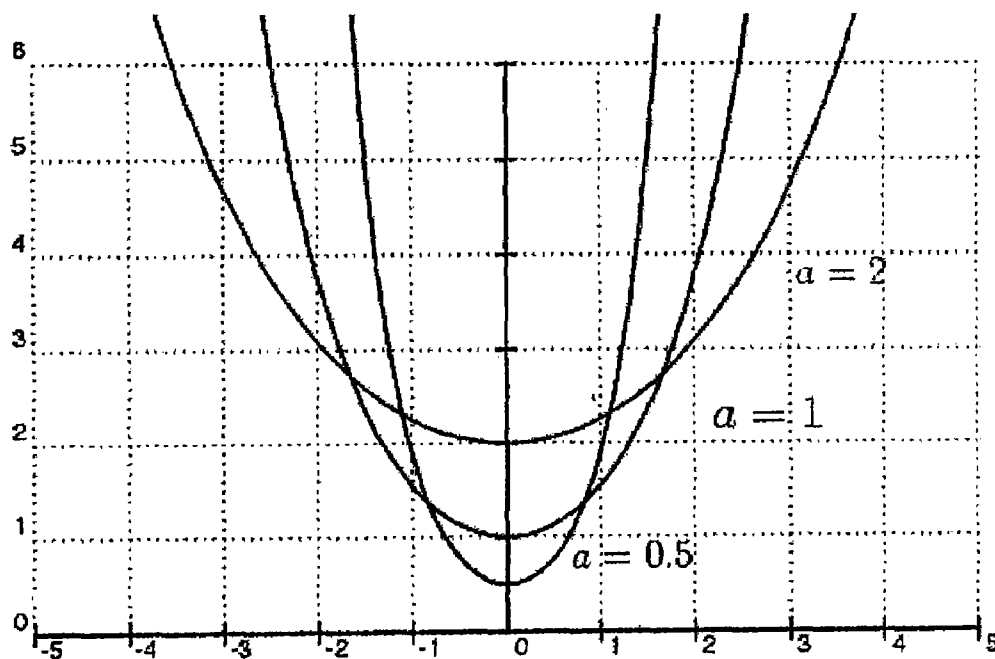


FIG. 3

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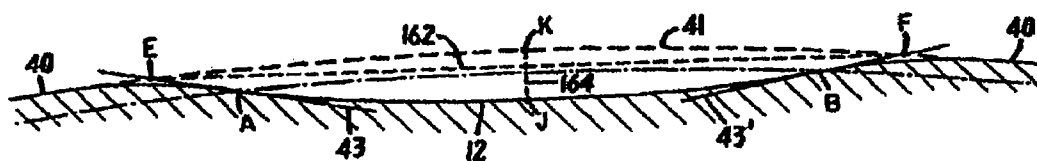


FIG. 4

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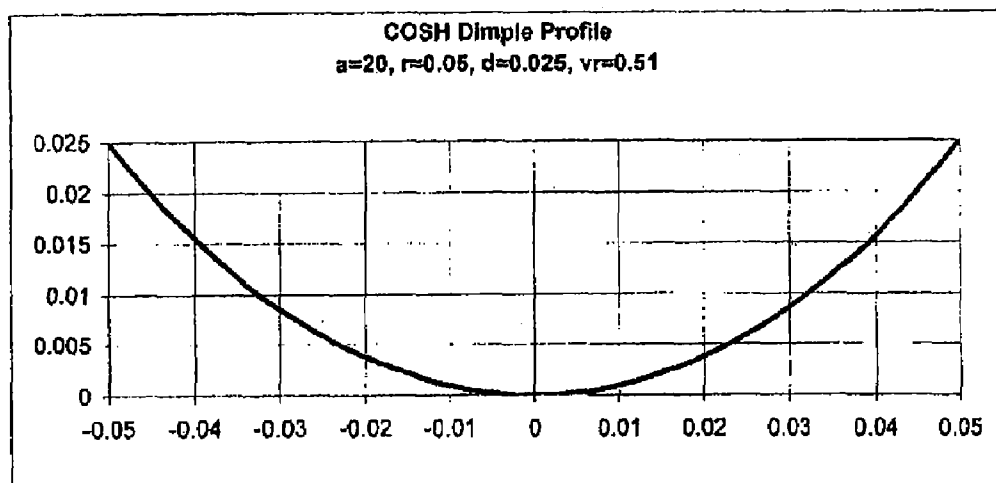


FIG. 5

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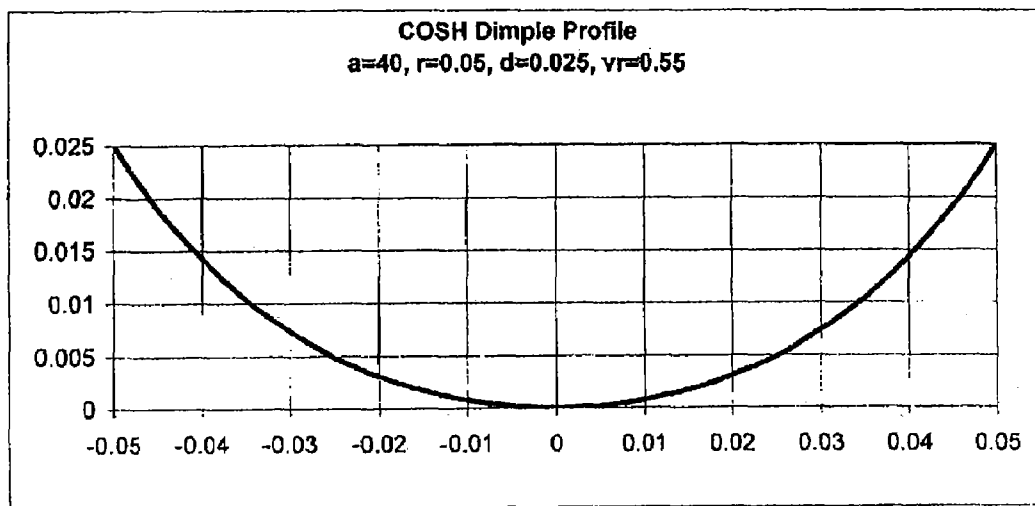


FIG. 6

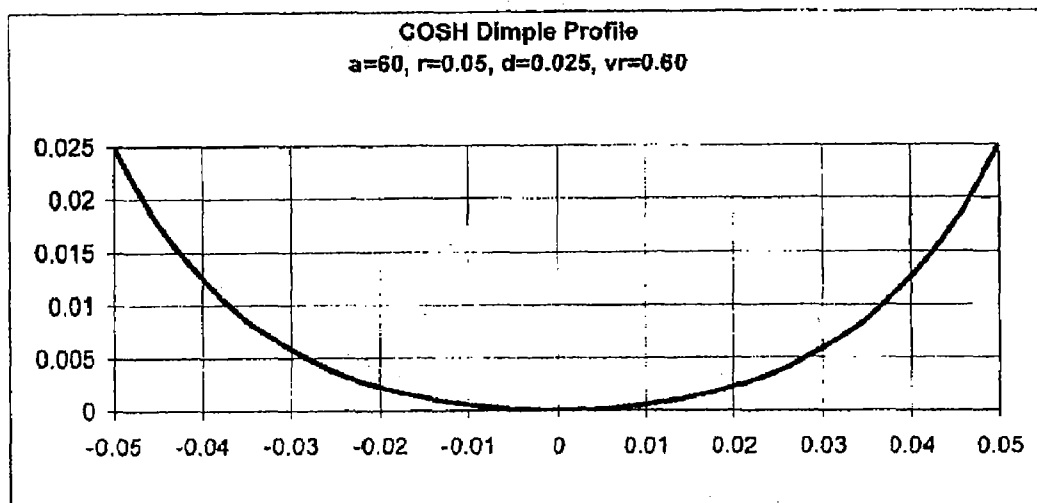


FIG. 7

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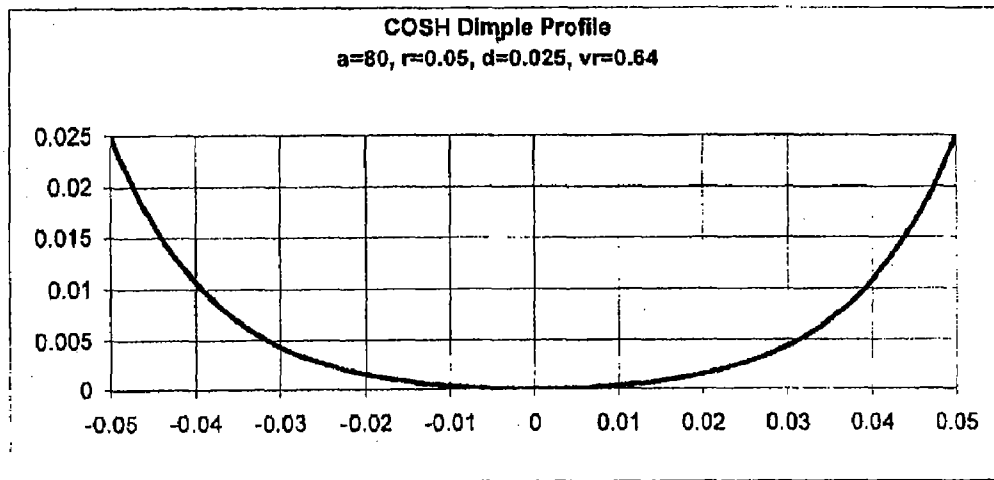


FIG. 8

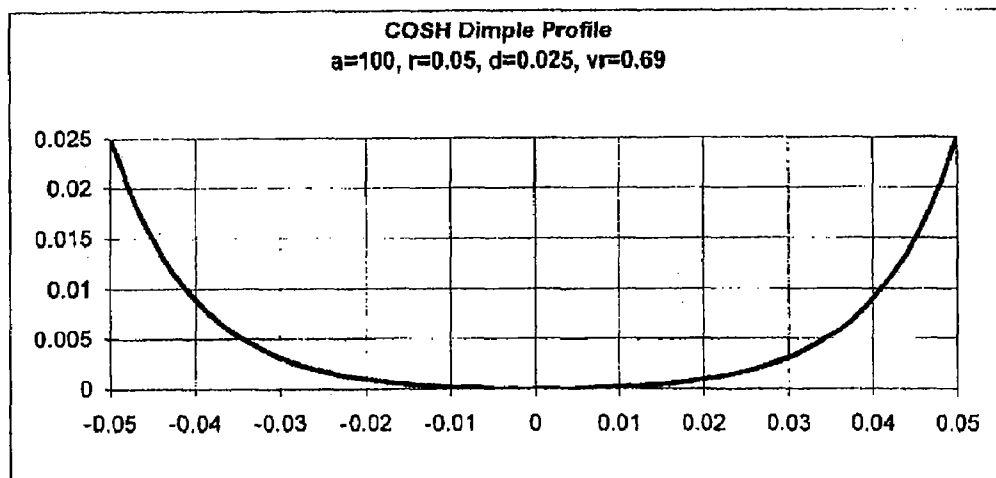
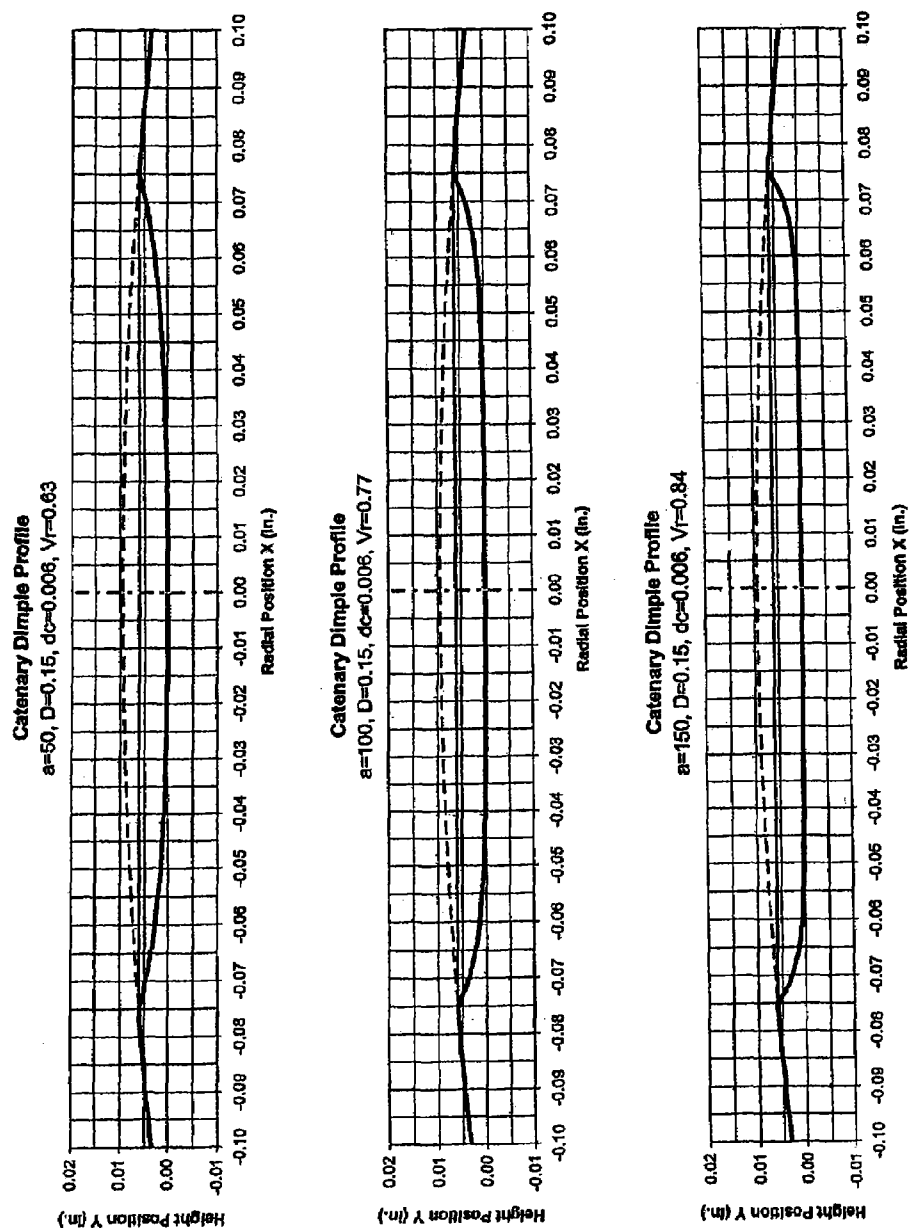
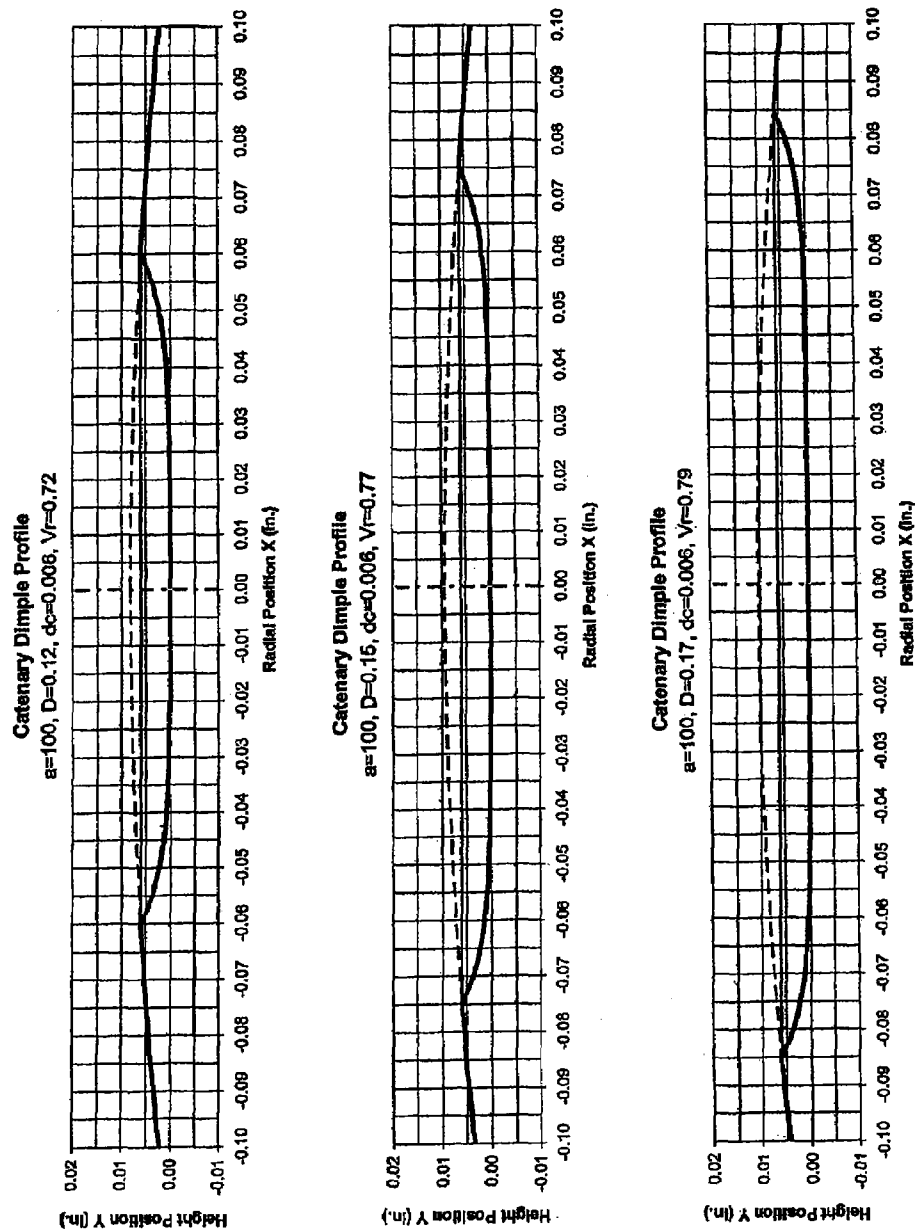


FIG. 9

**FIG. 10**

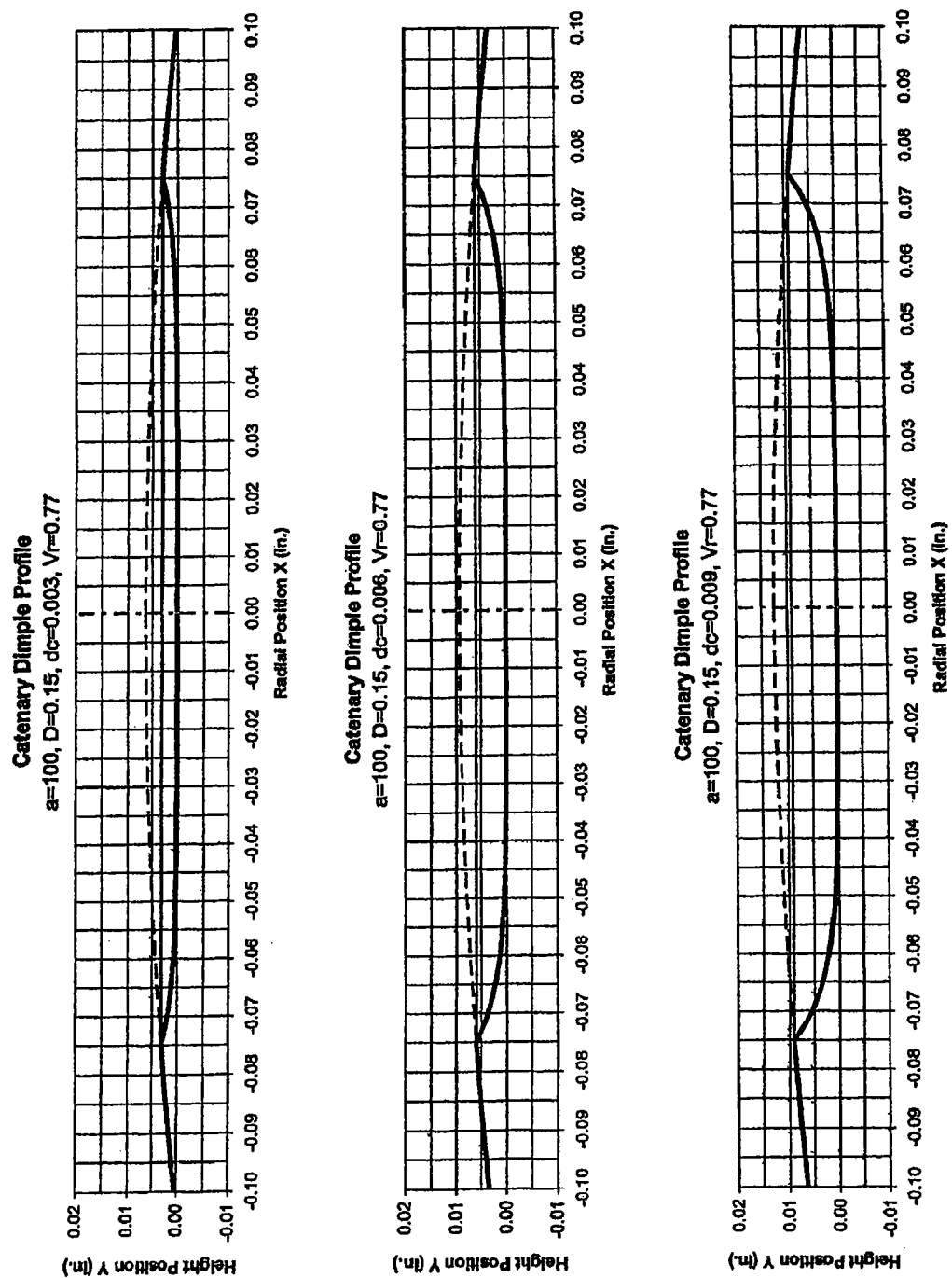
**FIG. 11**

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**FIG. 12**

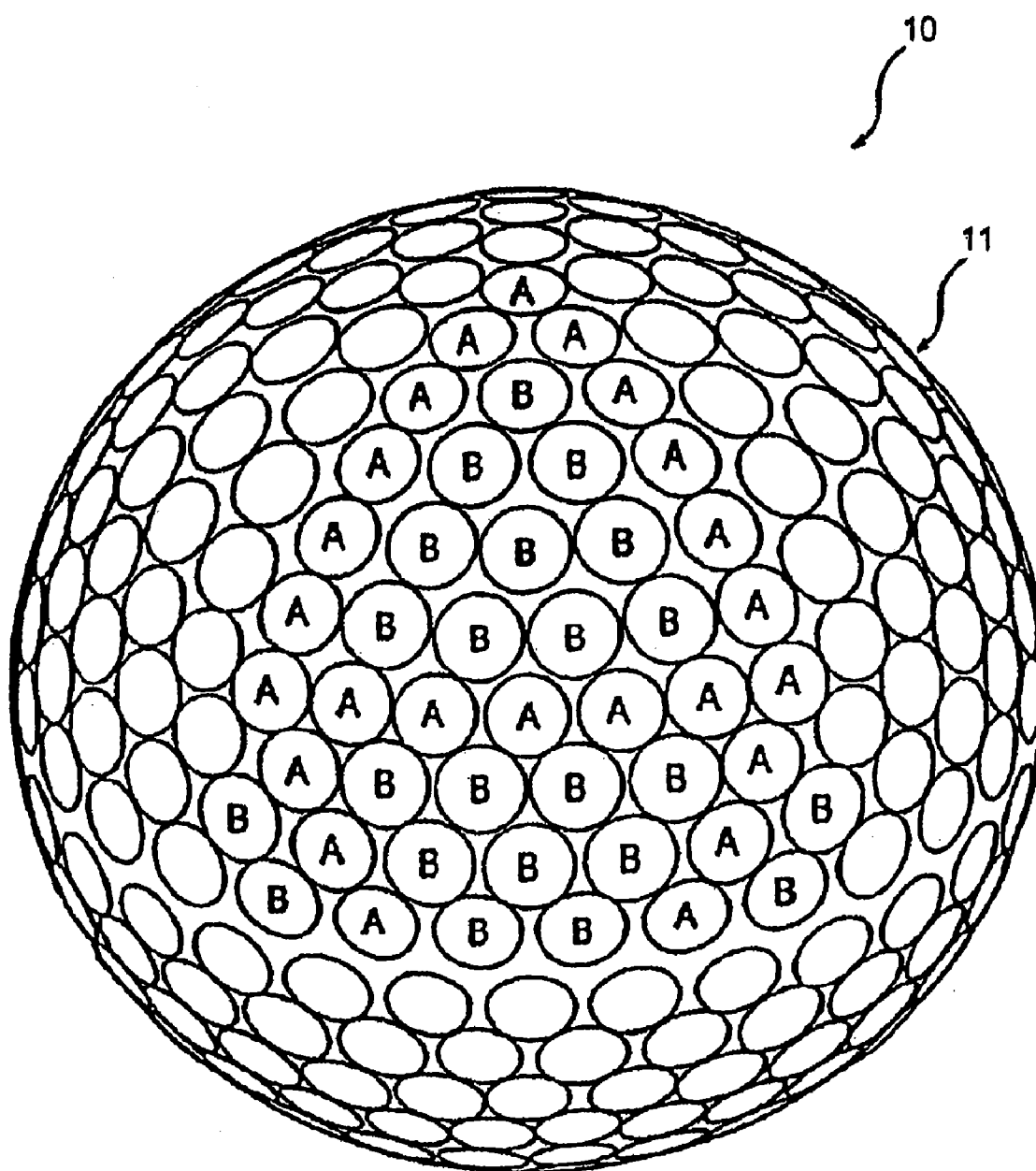


FIG. 13

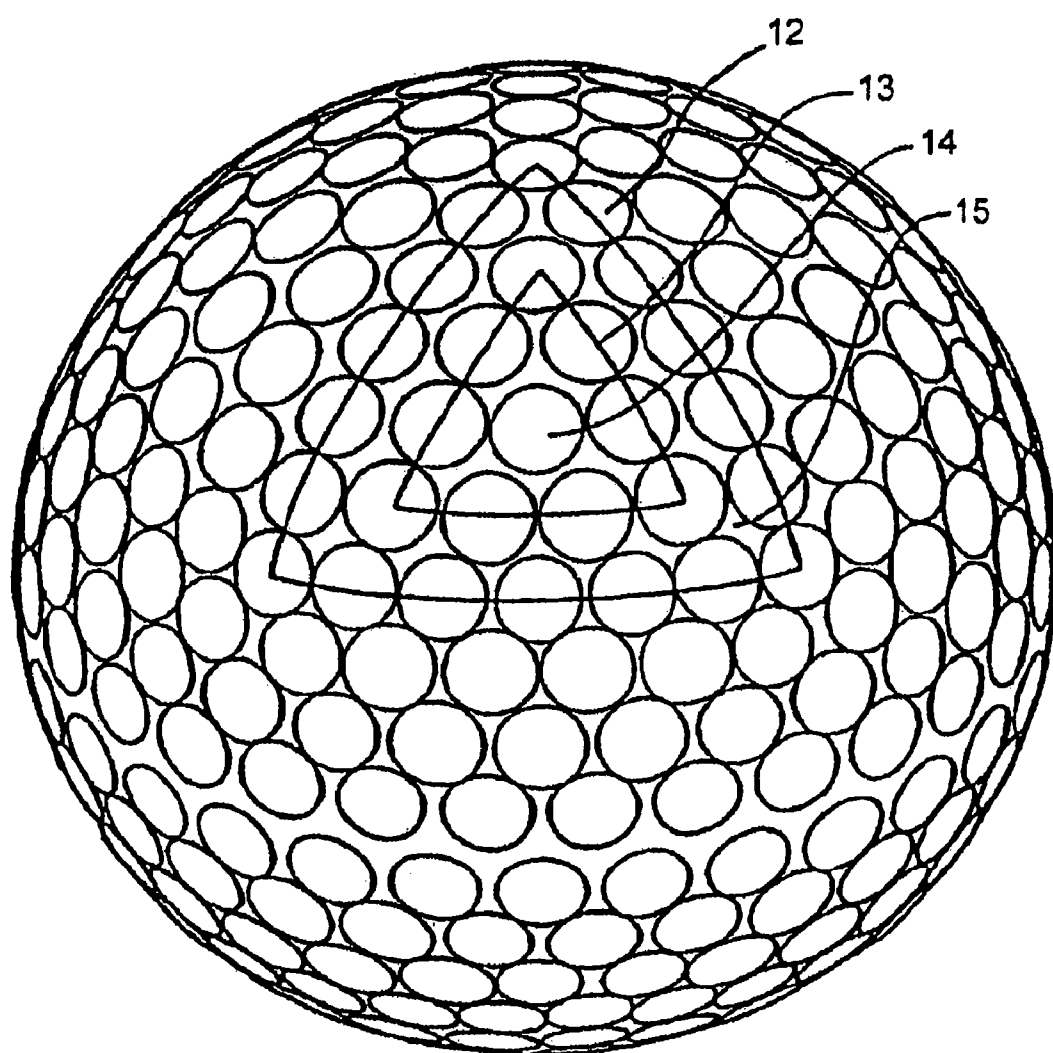
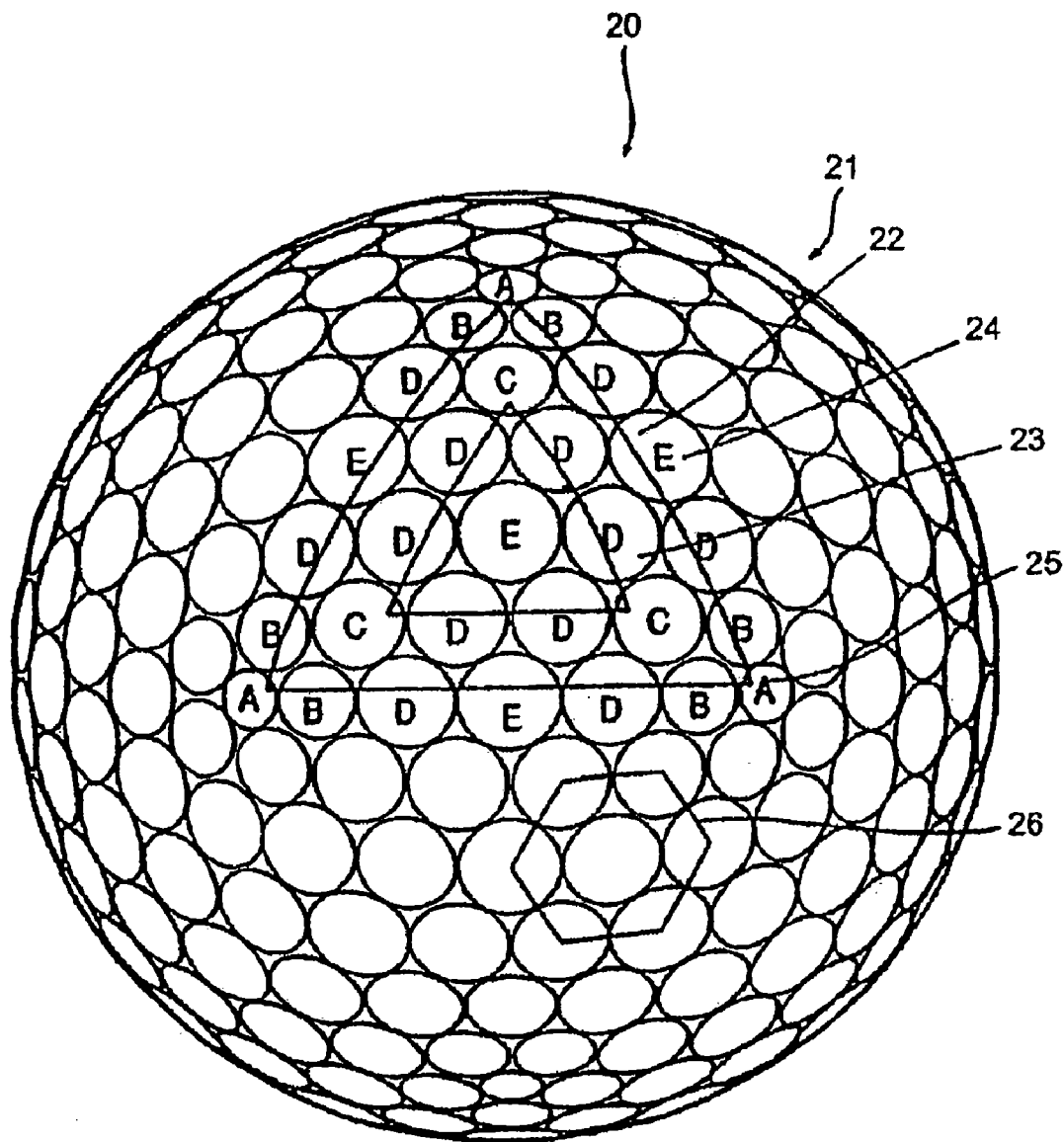


FIG. 14

$D_A < D_B \leq D_C \leq D_D \leq D_E$
 $80\% D_A, D_B, D_C, D_D, D_E > 0.11"$
 $\text{DIMP. AREA} > 80\%$

**FIG. 15**

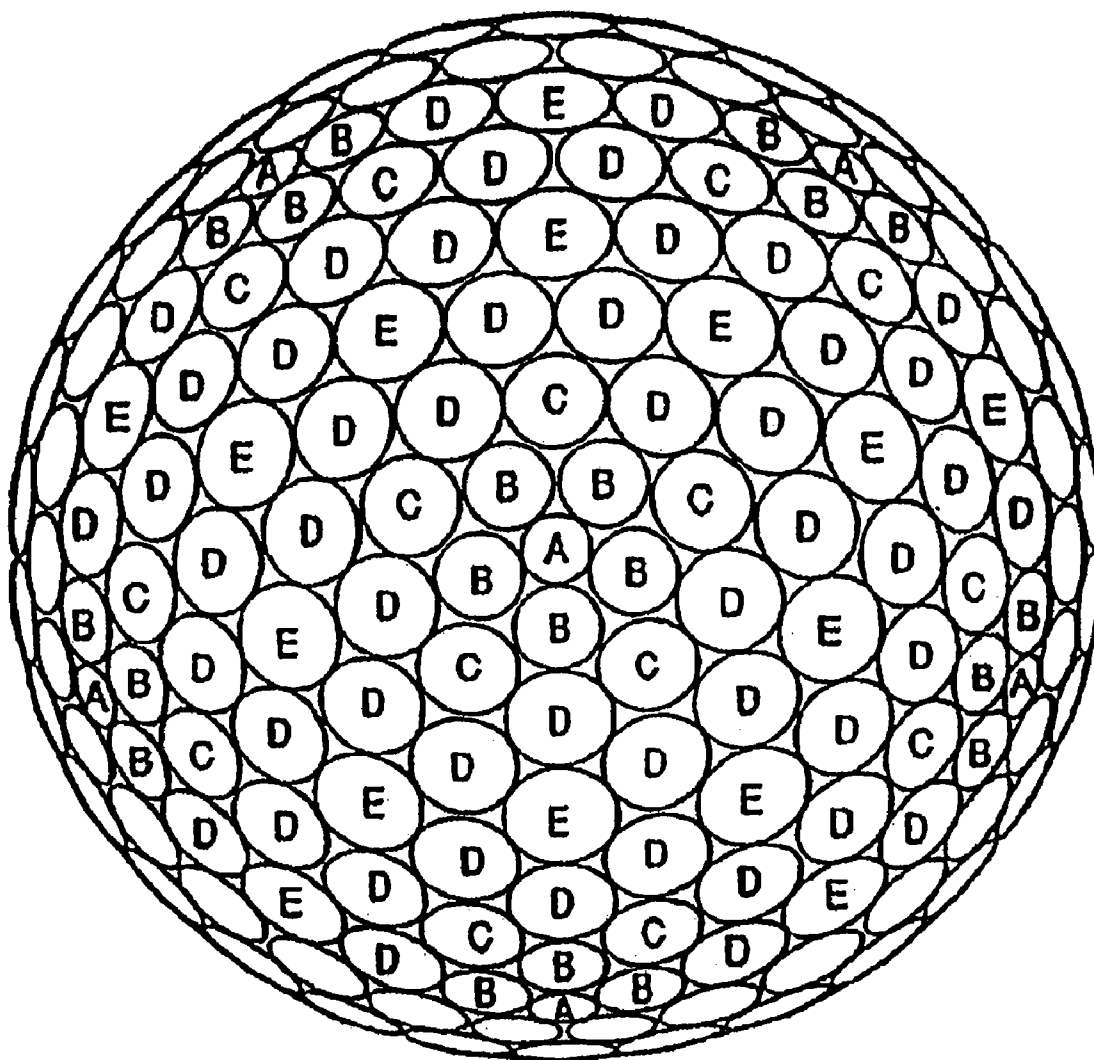


FIG. 16

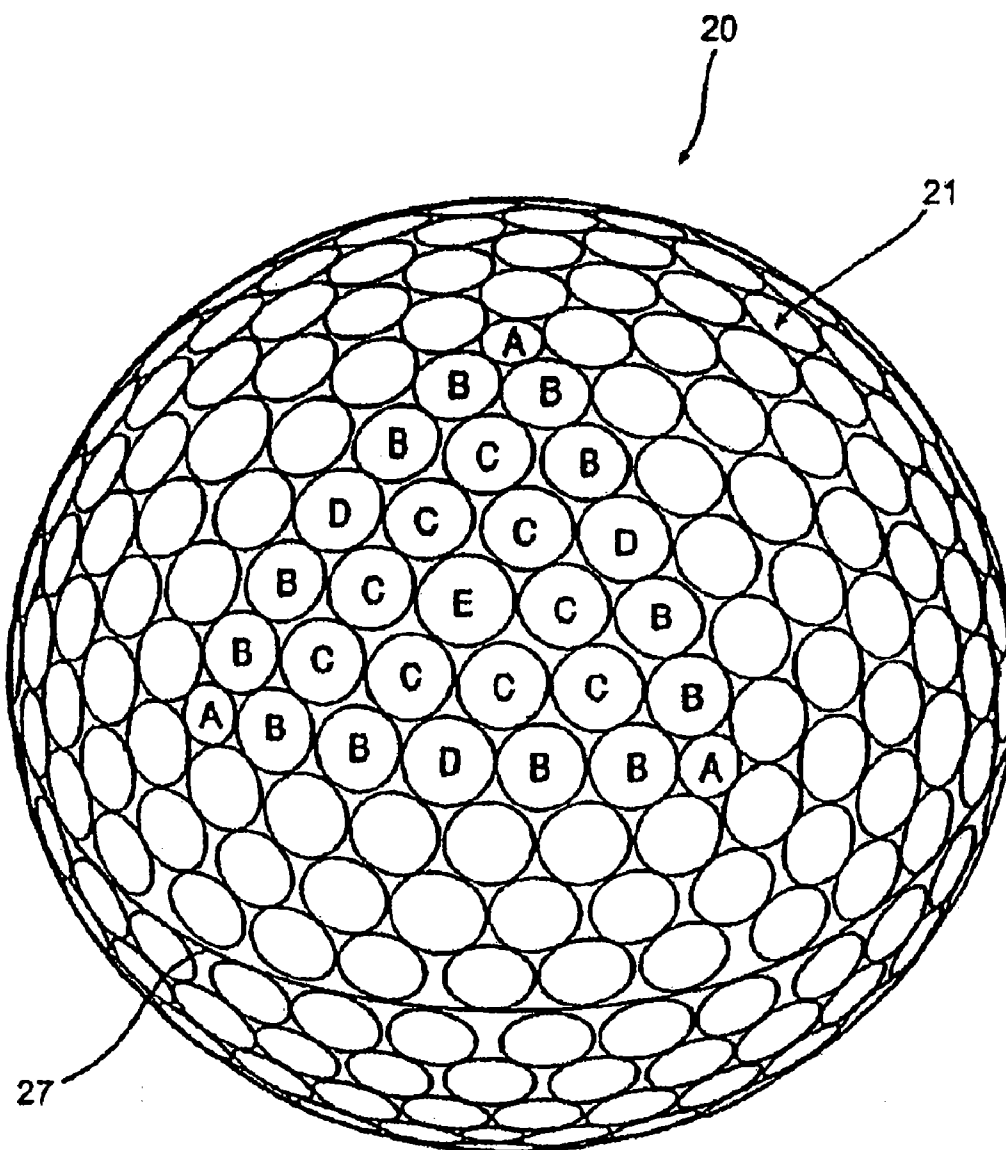


FIG. 17

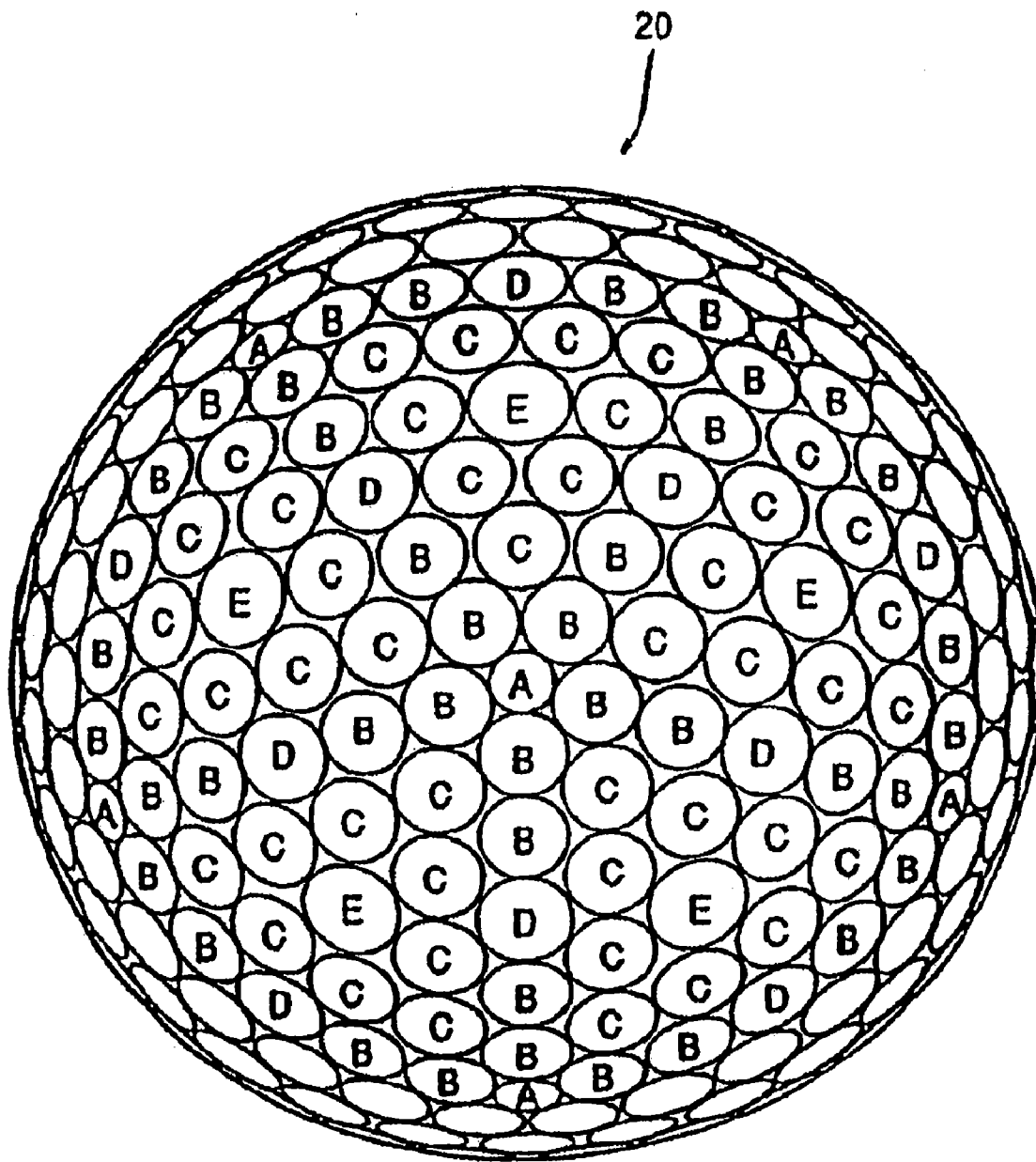


FIG. 18

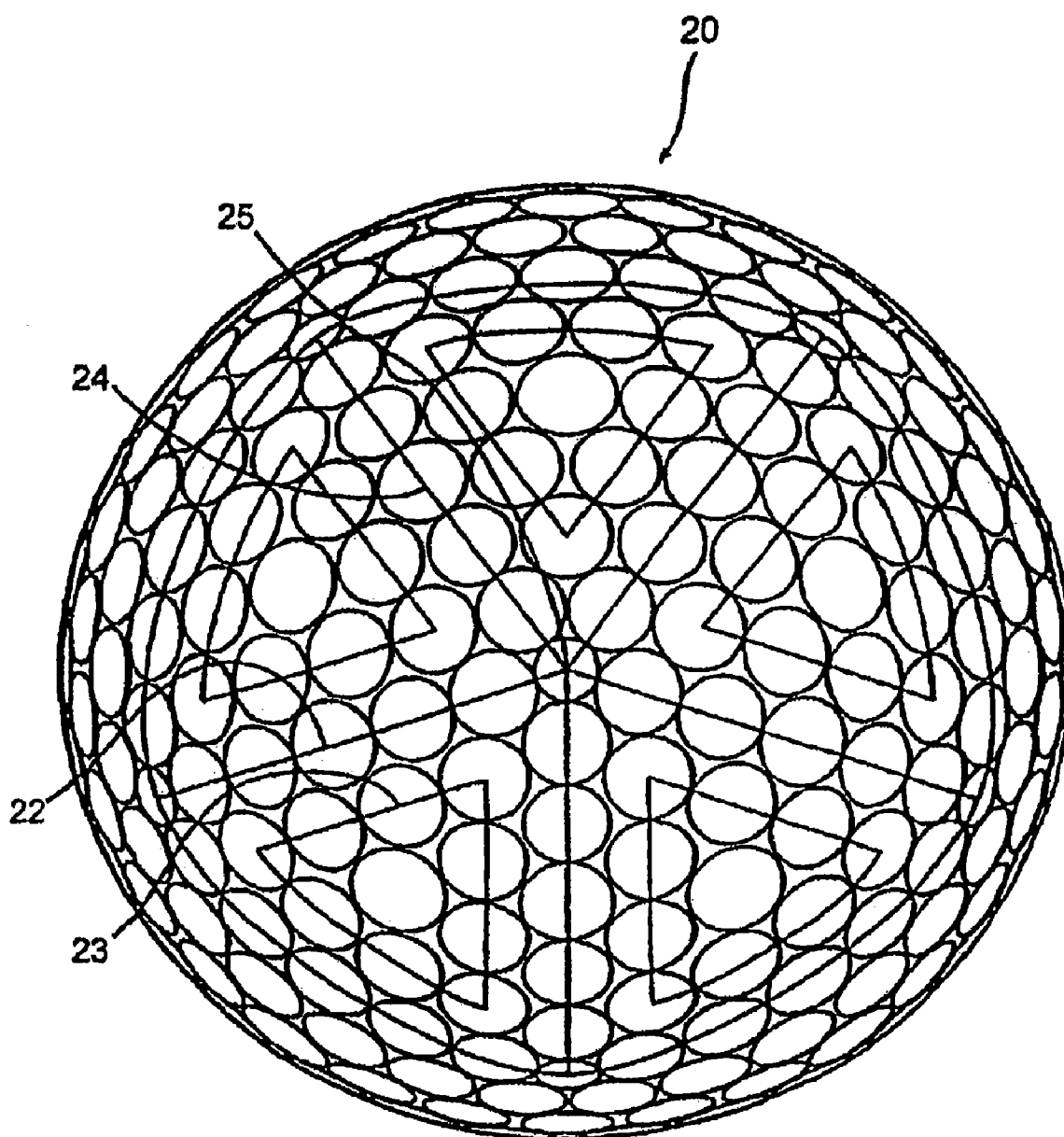


FIG. 19

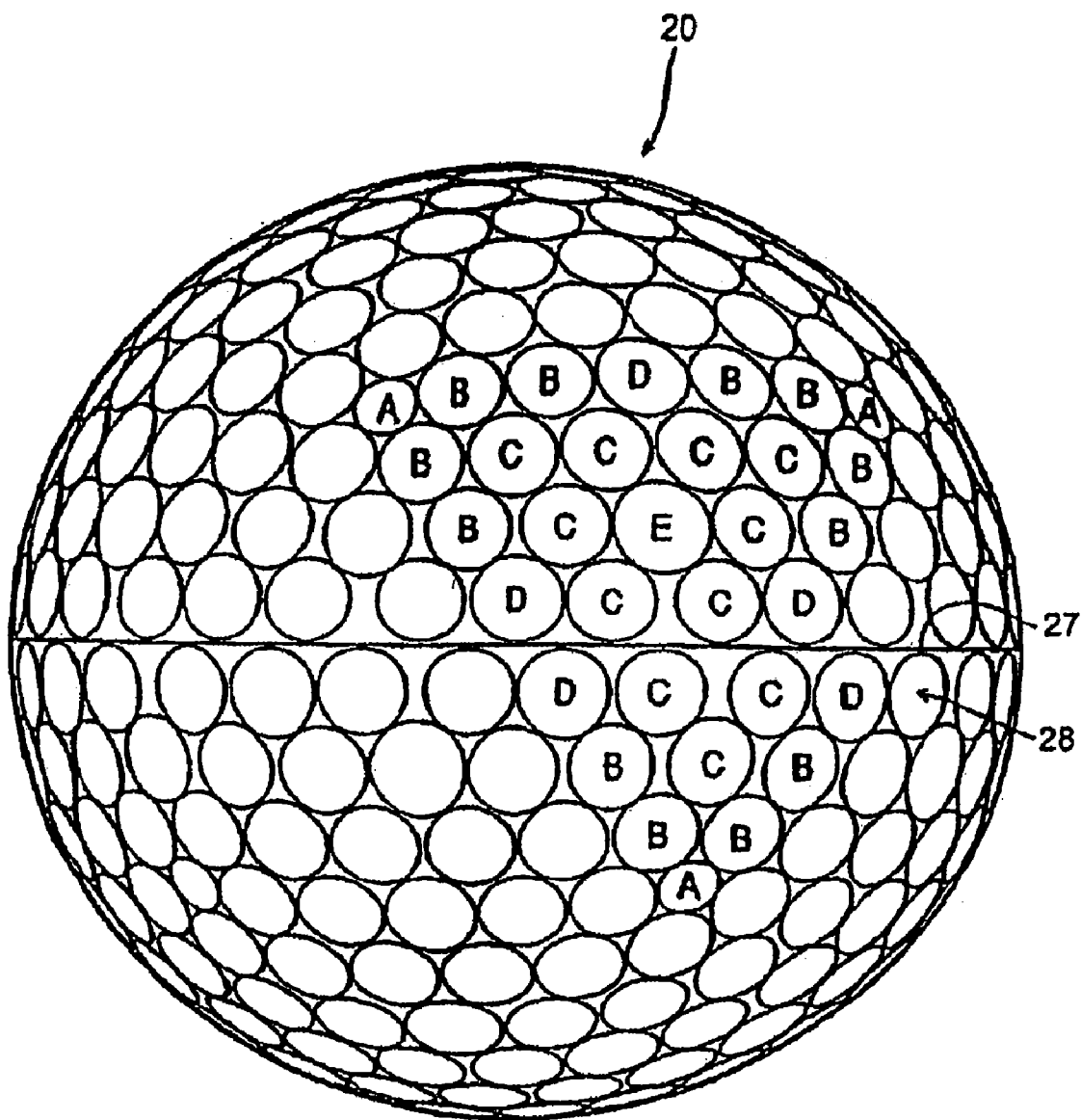


FIG. 20



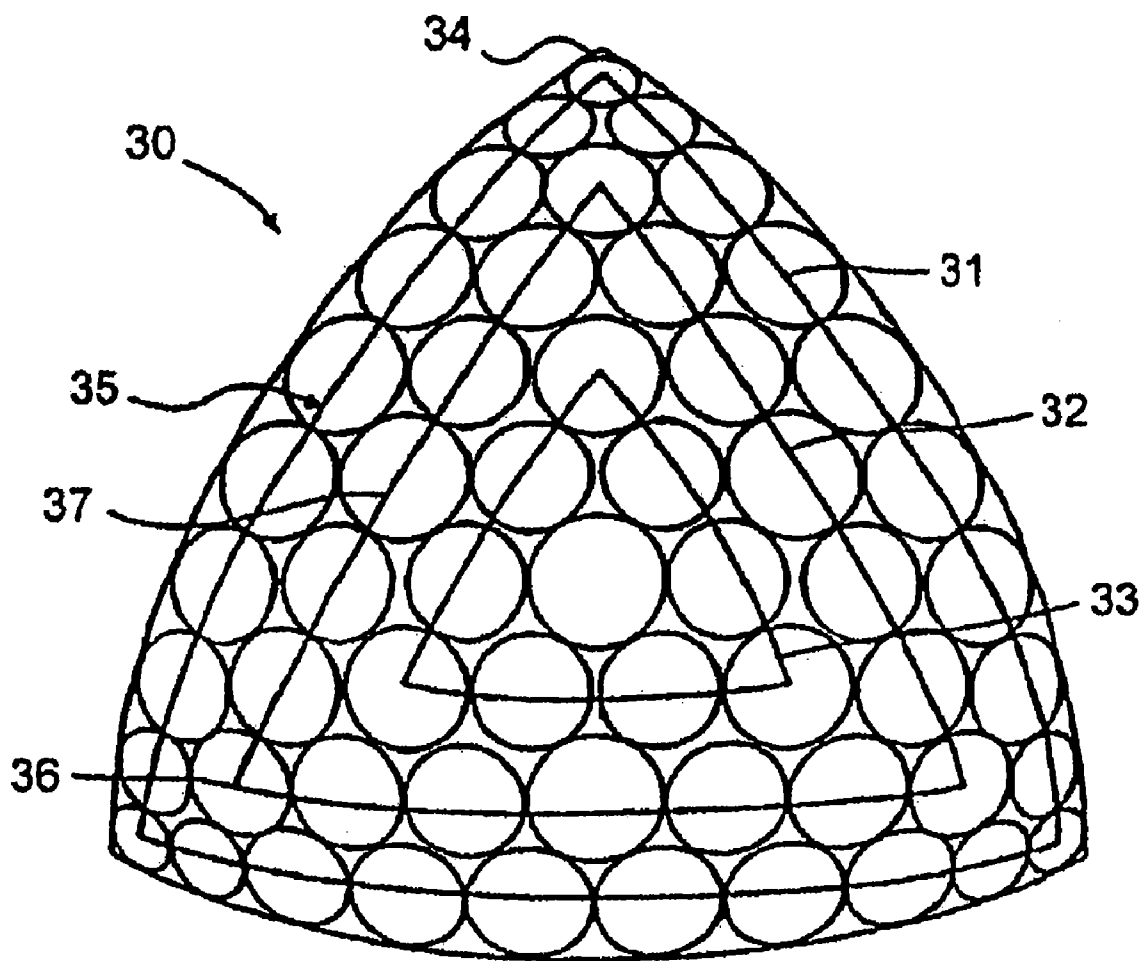
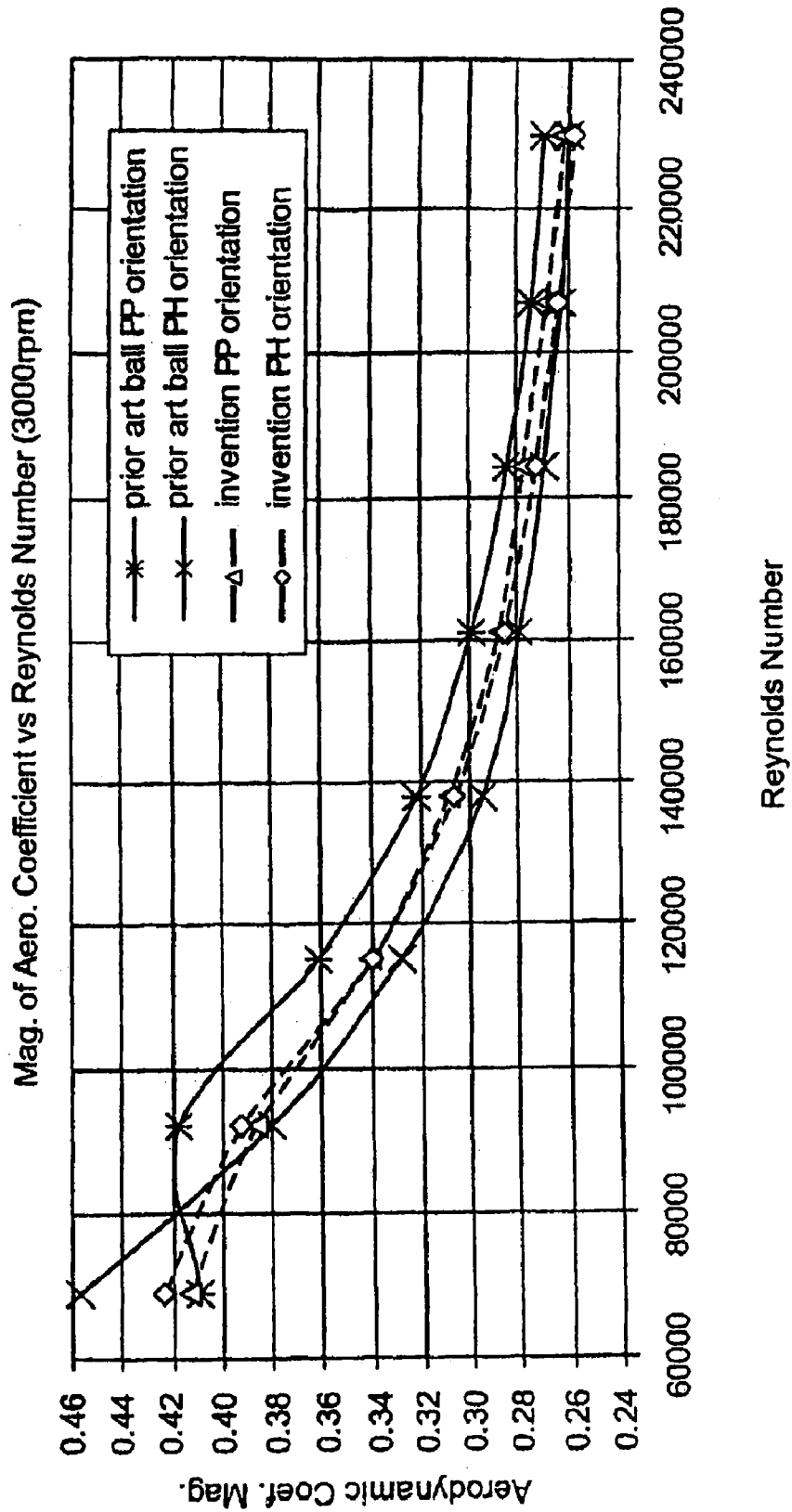
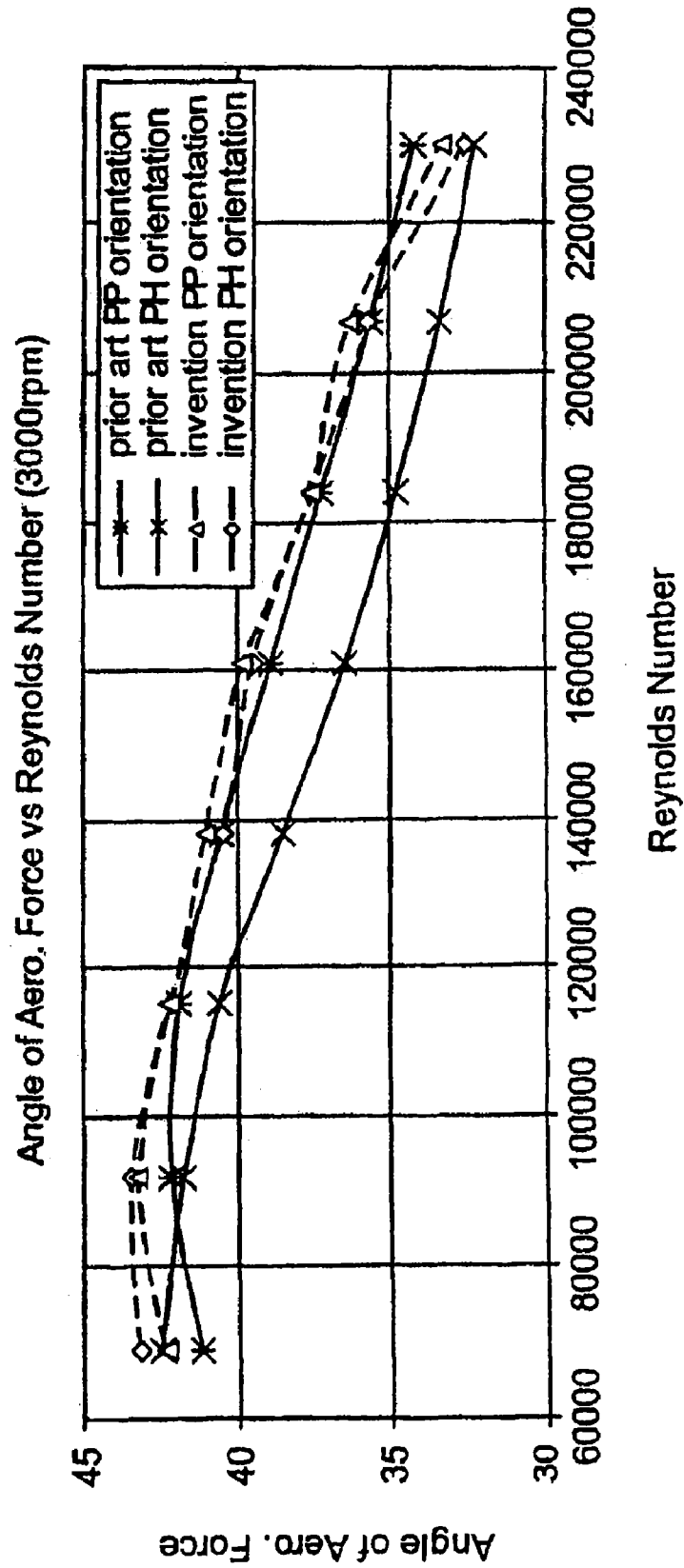


FIG. 22

**FIG. 23**

**FIG. 24**

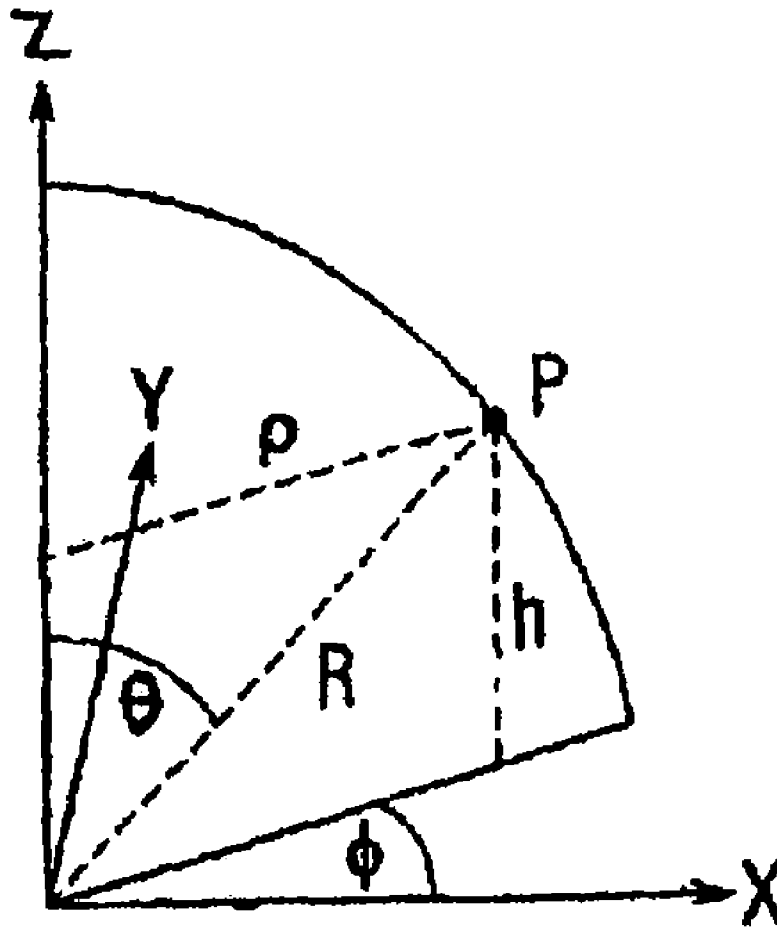


FIG. 25

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GOLF BALL DIMPLES WITH A CATENARY CURVE PROFILE**CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is a continuation of U.S. patent application Ser. No. 12/071,087, filed Feb. 15, 2008, now U.S. Pat. No. 7,641,572, which is a continuation-in-part of U.S. application Ser. No. 11/907,195, filed Oct. 10, 2007, now U.S. Pat. No. 7,491,137, which is a continuation of U.S. patent application Ser. No. 11/607,916 filed Dec. 4, 2006, now abandoned, which is a continuation of U.S. patent application Ser. No. 11/108,812 filed Apr. 19, 2005, now U.S. Pat. No. 7,156,757, which is a continuation of U.S. patent application Ser. No. 10/784,744, filed Feb. 24, 2004, now U.S. Pat. No. 6,913,550, which is a continuation of U.S. patent application Ser. No. 10/096,852, filed Mar. 14, 2002, now U.S. Pat. No. 6,729,976, which is a continuation-in-part of U.S. patent application Ser. No. 09/989,191, filed Nov. 21, 2001, now U.S. Pat. No. 6,796,912, and also a continuation-in-part of U.S. patent application Ser. No. 09/404,164, filed Sep. 27, 1999, now U.S. Pat. No. 6,358,161, which is a divisional of U.S. patent application Ser. No. 08/922,633, filed Sep. 3, 1997, now U.S. Pat. No. 5,957,786. The entire disclosures of the related applications are incorporated by reference herein.

FIELD OF INVENTION

The present invention relates to golf balls having improved aerodynamic characteristics that yield improved flight performance and longer ball flight. The improved aerodynamic characteristics are obtained through the use of specific dimple arrangements and dimple profiles. In particular, the invention relates to a dimple pattern including dimples having a cross-sectional profile defined by a mathematical function based on a catenary curve. The use of such a cross-sectional profile provides improved means to control dimple shape, volume, and transition to a spherical golf ball surface. The aerodynamic improvements are applicable to golf balls of any size and weight.

BACKGROUND OF THE INVENTION

The flight of a golf ball is determined by many factors. The majority of the properties that determine flight are outside of the control of the golfer. While a golfer can control the speed, the launch angle, and the spin rate of a golf ball by hitting the ball with a particular club, the final resting point of the ball depends upon golf ball construction and materials, as well as environmental conditions, e.g., terrain and weather. Since flight distance and consistency are critical factor in reducing golf scores, manufacturers continually strive to make even the slightest incremental improvements in golf ball flight consistency and flight distance, e.g., one or more yards, through various aerodynamic properties and golf ball constructions. For example, golf balls were originally made with smooth outer surfaces. However, in the late nineteenth century, players observed that, as golf balls became scuffed or marred from play, the balls achieved more distance. As such, players then began to roughen the surface of new golf balls with a hammer to increase flight distance.

Manufacturers soon caught on and began molding non-smooth outer surfaces on golf balls. By the mid 1900's, almost every golf ball being made had 336 dimples arranged in an octahedral pattern. Generally, these balls had about 60 percent of their outer surface covered by dimples. Over time,

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improvements in ball performance were developed by utilizing different dimple patterns. In 1983, for instance, Titleist introduced the TITLEIST 384, which had 384 dimples that were arranged in an icosahedral pattern resulting in about 76 percent coverage of the ball surface. The dimpled golf balls used today travel nearly two times farther than a similar ball without dimples.

These improvements have come at great cost to manufacturers. In fact, historically manufacturers improved flight performance via iterative testing, where golf balls with numerous dimple patterns and dimple profiles are produced and tested using mechanical golfers. Flight performance is characterized in these tests by measuring the landing position of the various ball designs. For example, to determine if a particular ball design has desirable flight characteristics for a broad range of players, i.e., high and low swing speed players, manufacturers perform the mechanical golfer test with different ball launch conditions, which involves immense time and financial commitments. Furthermore, it is difficult to identify incremental performance improvements using these methods due to the statistical noise generated by environmental conditions, which necessitates large sample sizes for sufficient confidence intervals.

Another more precise method of determining specific dimple arrangements and dimple shapes, that result in an aerodynamic advantage, involves the direct measurement of aerodynamic characteristics as opposed to ball landing positions. These aerodynamic characteristics define the forces acting upon the golf ball throughout flight.

Aerodynamic forces acting on a golf ball are typically resolved into orthogonal components of lift (F_L) and drag (F_D). FIG. 1 shows the various forces acting on a golf ball in flight. Lift is defined as the aerodynamic force component acting perpendicular to the flight path. It results from a difference in pressure that is created by a distortion in the air flow that results from the back spin of the ball. A boundary layer forms at the stagnation point of the ball, B, then grows and separates at points S1 and S2, as shown in FIG. 2. Due to the ball backspin, the top of the ball moves in the direction of the airflow, which retards the separation of the boundary layer. In contrast, the bottom of the ball moves against the direction of airflow, thus advancing the separation of the boundary layer at the bottom of the ball. Therefore, the position of separation of the boundary layer at the top of the ball, S1, is further back than the position of separation of the boundary layer at the bottom of the ball, S2. This asymmetrical separation creates an arch in the flow pattern, requiring the air over the top of the ball to move faster and, thus, have lower pressure than the air underneath the ball.

Drag is defined as the aerodynamic force component acting parallel to the ball flight direction. As the ball travels through the air, the air surrounding the ball has different velocities and, accordingly, different pressures. The air exerts maximum pressure at the stagnation point, B, on the front of the ball, as shown in FIG. 2. The air then flows over the sides of the ball and has increased velocity and reduced pressure. The air separates from the surface of the ball at points S1 and S2, leaving a large turbulent flow area with low pressure, i.e., the wake. The difference between the high pressure in front of the ball and the low pressure behind the ball reduces the ball speed and acts as the primary source of drag for a golf ball.

The dimples on a golf ball are important in reducing drag and increasing lift. For example, the dimples on a golf ball create a turbulent boundary layer around the ball, i.e., the air in a thin layer adjacent to the ball flows in a turbulent manner. The turbulence energizes the boundary layer and helps it stay

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attached further around the ball to reduce the area of the wake. This greatly increases the pressure behind the ball and substantially reduces the drag.

Based on the role that dimples play in reducing drag on a golf ball, golf ball manufacturers continually seek dimple patterns that increase the distance traveled by a golf ball. A high degree of dimple coverage is beneficial to flight distance, but only if the dimples are of a reasonable size. Dimple coverage gained by filling spaces with tiny dimples is not very effective, since tiny dimples are not good turbulence generators.

In addition to researching dimple pattern and size, golf ball manufacturers also study the effect of dimple shape, volume, and cross-section on overall flight performance of the ball. One example is U.S. Pat. No. 5,735,757, which discusses making dimples using two different spherical radii with an "inflection point" where the two curves meet. In most cases, however, the cross-sectional profiles of dimples in prior art golf balls are spherical, parabolic, elliptical, semi-spherical curves, saucer-shaped, a sine curve, a truncated cone, or a flattened trapezoid. One disadvantage of these shapes is that they can sharply intrude into the surface of the ball, which may cause the drag to become excessive. As a result, the ball may not make best use of momentum initially imparted thereto, resulting in an insufficient carry of the ball.

Further, the most commonly used spherical profile is essentially a function of two parameters: diameter and depth (chordal or surface). While edge angle, which is a measure of the steepness of the dimple wall where it abuts the ball surface, is often discussed when describing these types of profiles, edge angle generally cannot be varied independently of depth unless dual radius profiles are employed. The cross sections of dual radius dimple profiles are generally defined by two circular arcs: the first arc defines the outer part of the dimple and the second arc defines the central part of the profile. The radii are typically larger in the center, which produces a saucer shaped dimple where the steepness of the walls (and, thus, the edge angle) may be varied independently of the dimple depth and diameter. While effective, this profile is described by a number of equations that at least require first order continuity for tangency between the arcs, as well as varying dimple diameter and depth values to achieve the desired dimple shape.

In addition to the profiles discussed above, dimple patterns have been employed in an effort to control and/or adjust the aerodynamic forces acting on a golf ball. For example, U.S. Pat. Nos. 6,213,898 and 6,290,615 disclose golf ball dimple patterns that reduce high-speed drag and increase low speed lift. It has now been discovered, however, contrary to the disclosures of these patents, that reduced high-speed drag and increased low speed lift does not necessarily result in improved flight performance. For example, excessive high-speed lift or excessive low-speed drag may result in undesirable flight performance characteristics. The prior art is silent, however, as to aerodynamic features that influence other aspects of golf ball flight, such as flight consistency, as well as enhanced aerodynamic coefficients for balls of varying size and weight.

Thus, there remains a need to optimize the aerodynamics of a golf ball to improve flight distance and consistency. Further, there is a need to develop dimple arrangements and profiles that result in longer distance and more consistent flights regardless of the swing-speed of a player, the orientation of the ball when impacted, or the physical properties of the ball being played. The use of catenary dimple profiles is considered one way to achieve these objectives.

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SUMMARY OF THE INVENTION

The present invention is directed to a golf ball having a plurality of recessed dimples on the surface thereof, wherein at least a portion of the plurality of recessed dimples have a profile defined by the revolution of a catenary curve according to the following function:

$$y = \frac{d_c (\cosh(sf * x) - 1)}{\cosh\left(sf * \frac{D}{2}\right) - 1}$$

wherein y is the vertical direction coordinate away from the center of the ball with 0 at the center of the dimple;

x is the horizontal (radial) direction coordinate from the dimple apex to the dimple surface with 0 at the center of the dimple;

sf is a shape factor;

d_c is the chordal depth of the dimple; and

D is the diameter of the dimple.

In one embodiment, about 50 percent or more of the dimples on the golf ball are defined by the catenary curve expression above. In another embodiment, about 80 percent or more of the dimples on the golf ball are defined by the catenary curve expression. In this aspect of the invention, D may range from about 0.100 inches to about 0.225 inches, sf from about 5 to about 200, and d_c from about 0.002 inches to about 0.008 inches. For example, D may be from about 0.115 inches to about 0.185 inches, sf from about 10 to about 100 or from about 10 to about 75, and d_c from about 0.004 inches to about 0.006 inches. In one embodiment, D is from about 0.115 inches to about 0.185 inches, sf is from about 10 to 100, and d_c is from about 0.004 inches to about 0.006 inches.

The golf ball may also include a plurality of dimples having an aerodynamic coefficient magnitude defined by $C_{mag} = \sqrt{(C_L^2 + C_D^2)}$ and an aerodynamic force angle defined by $\text{Angle} = \tan^{-1}(C_L/C_D)$, wherein C_L is a lift coefficient and C_D is a drag coefficient, wherein the golf ball includes: a first aerodynamic coefficient magnitude between about 0.24 and about 0.29 and a first aerodynamic force angle between about 32 degrees and about 39 degrees at a Reynolds Number of about 230000 and a spin ratio of about 0.080; and a second aerodynamic coefficient magnitude between about 0.24 and about 0.29 and a second aerodynamic force angle between about 33 degrees and about 41 degrees at a Reynolds Number of about 208000 and a spin ratio of about 0.090.

In this regard, the golf ball may also include a third aerodynamic coefficient magnitude between about 0.25 and about 0.30 and a third aerodynamic force angle between about 34 degrees and about 42 degrees at a Reynolds Number of about 190000 and a spin ratio of about 0.10; and a fourth aerodynamic coefficient magnitude between about 0.25 and about 0.31 and a fourth aerodynamic force angle between about 35 degrees and about 43 degrees at a Reynolds Number of about 170000 and a spin ratio of about 0.11.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other aspects of the present invention may be more fully understood with reference to, but not limited by, the following drawings.

FIG. 1 is an illustration of the forces acting on a golf ball in flight;

FIG. 2 is an illustration of the air flow around a golf ball in flight;

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FIG. 3 is a graphical interpretation of a catenary curve with different values of the parameter a .

FIG. 4 shows a method for measuring the depth, diameter (twice the radius), and edge angle of a dimple;

FIG. 5 is a dimple cross-sectional profile defined by a hyperbolic cosine function, \cosh , with a shape constant of 20, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.51;

FIG. 6 is a dimple cross-sectional profile defined by a hyperbolic cosine function, \cosh , with a shape constant of 40, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.55;

FIG. 7 is a dimple cross-sectional profile defined by a hyperbolic cosine function, \cosh , with a shape constant of 60, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.60;

FIG. 8 is a dimple cross-sectional profile defined by a hyperbolic cosine function, \cosh , with a shape constant of 80, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.64;

FIG. 9 is a dimple cross-sectional profile defined by a hyperbolic cosine function, \cosh , with a shape constant of 100, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.69;

FIG. 10 illustrates dimple cross-sectional profiles that are defined by a hyperbolic cosine function, \cosh , with varying shape constants, a dimple diameter of 0.150 inches, and a dimple chordal depth of 0.006 inches;

FIG. 11 illustrates dimple cross-sectional profiles that are defined by a hyperbolic cosine function, \cosh , with varying dimple diameters, a shape factor of 100, and a dimple chordal depth of 0.006 inches;

FIG. 12 illustrates dimple cross-sectional profiles that are defined by a hyperbolic cosine function, \cosh , with varying dimple chordal depths, a shape factor of 100, and a dimple diameter of 0.150 inches;

FIG. 13 is an isometric view of the icosahedron pattern used on a golf ball;

FIG. 14 is an isometric view of the icosahedron pattern used on a golf ball showing the triangular regions formed by the icosahedron pattern;

FIG. 15 is an isometric view of a golf ball according to the present invention having an icosahedron pattern, showing dimple sizes;

FIG. 16 is a top view of the golf ball in FIG. 15, showing dimple sizes and arrangement;

FIG. 17 is an isometric view of another embodiment of a golf ball according to the present invention having an icosahedron pattern, showing dimple sizes and the triangular regions formed from the icosahedron pattern;

FIG. 18 is a top view of the golf ball in FIG. 17, showing dimple sizes and arrangement;

FIG. 19 is a top view of the golf ball in FIG. 17, showing dimple arrangement;

FIG. 20 is a side view of the golf ball in FIG. 17, showing the dimple arrangement at the equator;

FIG. 21 is a spherical-triangular region of a golf ball according to the present invention having an octahedral dimple pattern, showing dimple sizes;

FIG. 22 is the spherical triangular region of FIG. 21, showing the triangular dimple arrangement;

FIG. 23 is a graph of the magnitude of aerodynamic coefficients versus Reynolds Number for a golf ball made according to the present invention and a prior art golf ball;

FIG. 24 is a graph of the angle of aerodynamic force versus Reynolds Number for a golf ball made according to the present invention and a prior art golf ball; and

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FIG. 25 is a graph illustrating the coordinate system in a dimple pattern according to one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to golf balls having improved aerodynamic performance due, at least in part, to the selection of dimple arrangements and dimple profiles. In particular, the present invention is directed to a golf ball that includes at least a portion of its dimples that are defined by the revolution of a catenary curve about an axis.

The dimple profiles of the present invention may be used with practically any type of ball construction. For instance, the golf ball may have a two-piece design, a double cover, or veneer cover construction depending on the type of performance desired of the ball. Other suitable golf ball constructions include solid, wound, liquid-filled, and/or dual cores, and multiple intermediate layers. Examples of these and other types of ball constructions that may be used with the present invention include those described in U.S. Pat. Nos. 5,713,801, 5,803,831, 5,885,172, 5,919,100, 5,965,669, 5,981,654, 5,981,658, and 6,149,535, as well as in Publication No. US2001/0009310 A1.

Different materials may be used in the construction of the golf balls made with the present invention. For example, the cover of the ball may be made of a thermoset or thermoplastic, a castable or non-castable polyurethane and polyurea, an ionomer resin, balata, or any other suitable cover material known to those skilled in the art. Conventional and non-conventional materials may be used for forming core and intermediate layers of the ball including polybutadiene and other rubber-based core formulations, ionomer resins, highly neutralized polymers, and the like.

After selecting the desired ball construction, the flight performance of the golf ball can be adjusted according to the design, placement, and number of dimples on the ball. As explained in greater detail below, the use of catenary curves provides a relatively effective way to modify the ball flight performance without significantly altering the dimple pattern and, thus, allow greater flexibility to ball designers to better customize a golf ball to suit a player.

Dimple Profiles of the Invention

A catenary curve represents the assumed shape of a perfectly flexible, uniformly dense, and inextensible chain suspended from its endpoints. In general, the mathematical formula representing such a curve is expressed as equation (1):

$$y = a \cosh\left(\frac{x}{a}\right) \quad (1)$$

where a is a constant in terms of horizontal tension in the chain and its weight per unit length, y is the vertical axis and x is the horizontal axis in a two dimensional Cartesian space. The chain is steepest near the points of suspension because this part of the chain has the most weight pulling down on it. Toward the bottom, the slope of the chain decreases because the chain is supporting less weight. FIG. 3 generally demonstrates the concept of a catenary curve with different values of the parameter a .

The present invention is directed to defining dimples on a golf ball by revolving a catenary curve about its y axis. In particular, the catenary curve used to define a golf ball dimple is a hyperbolic cosine function in the form of:

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$$y = \frac{d_c(\cosh(sf * x) - 1)}{\cosh\left(sf * \frac{D}{2}\right) - 1} \quad (2)$$

where: y is the vertical direction coordinate with 0 at the bottom of the dimple and positive upward (away from the center of the ball);

x is the horizontal (radial) direction coordinate, with 0 at the center of the dimple;

sf is a shape constant (also called shape factor);

d_c is the chordal depth of the dimple; and

D is the diameter of the dimple.

Unlike the dual radius dimple profile discussed previously, the inventive dimple profiles based on catenary curves are defined by a single continuous, differentiable function having independent variables of dimple diameter, depth, and shape factor (relative curvature and edge angle). Thus, the dimple profiles of the present invention can have any combination of diameter, depth, and edge angle with no additional requirements on derivatives of the function used to define the dimple profile.

The “shape constant” or “shape factor”, sf, is an independent variable in the mathematical expressions described above for a catenary curve. The use of a shape factor in the present invention provides an expedient method of generating alternative dimple profiles, for dimples with fixed radii and depth. For example, the shape factor may be used to independently alter the volume ratio (V_r) of the dimple while holding the dimple depth and radius fixed. The volume ratio is the ratio of the chordal dimple volume (bounded by the dimple surface and its chord plane divided by the volume of a cylinder defined by a similar diameter and chordal depth as the dimple). Accordingly, if a golf ball designer desires to generate balls with alternative lift and drag characteristics for a particular dimple position, diameter, and depth, then the golf ball designer may simply describe alternative shape factors to obtain alternative lift and drag performance without having to change these other parameters. No modification to the dimple layout on the surface of the ball is required.

Similar changes in the volume ratio and aerodynamic performance may be accomplished by using alternate forms of the equation (2) above to define the catenary dimple profile, see, e.g., equations (5), (6), (7), and (8) below.

While the present invention is directed toward using a catenary curve for at least a portion of the dimples on a golf ball, it is not necessary that catenary curves be used on every dimple on a golf ball. In some cases, the use of a catenary curve may only be used for a small number of dimples. Alternatively, a large amount of dimples may have profiles based on a catenary curve. In general, it is preferred that a sufficient number of dimples on the ball have catenary curves so that variation of shape factors will allow a designer to alter the flight characteristics of the ball. Thus, in one embodiment, at least about 30 percent, preferably about 50 percent, and more preferably at least about 60 percent, of the dimples on a golf ball are defined by a catenary curve.

Accordingly, the present invention uses variations of equation (2) to define the cross-section of at least a portion of the dimples on a golf ball. For example, the catenary curve can be defined by hyperbolic sine or cosine functions, ratios of these functions or combinations of them. A hyperbolic sine function is defined by the following expression:

$$\sinh(x) = \frac{e^x - e^{-x}}{2} \quad (3)$$

while a hyperbolic cosine function is defined by the following expression:

$$\cosh(x) = \frac{e^x + e^{-x}}{2}. \quad (4)$$

In one embodiment of the present invention, the mathematical equation for describing the cross-sectional profile of a dimple is expressed using the above expression by the following formula:

$$y = \frac{d_c(e^{(sf^2)} + e^{-(sf^2)} - 2)}{e^{(sf^2 \frac{D}{2})} + e^{-(sf^2 \frac{D}{2})} - 2} \quad (5)$$

where: y is the vertical direction coordinate with 0 at the bottom of the dimple and positive upward (away from the center of the ball);

x is the horizontal (radial) direction coordinate, with 0 at the center of the dimple;

sf is a shape factor;

d_c is the chordal depth of the dimple; and

D is the diameter of the dimple.

An alternate embodiment of the present invention involves a mathematical expression in terms of hyperbolic sine using the following formula:

$$y = \frac{d_c(\sqrt{1 + \sinh^2(sf * x)} - 1)}{\sqrt{1 + \sinh^2\left(sf * \frac{D}{2}\right)} - 1} \quad (6)$$

where y, x, sf, d_c , and D are defined as shown above.

In another embodiment of the present invention, a mathematical expression is shown as terms of a series expansion of one of the previous embodiments. However, the formula is preferably restricted to small values of sf, e.g., where sf is less than or equal to about 50. The equation describing the cross-sectional profile is expressed by the following formula:

$$y = \frac{d_c sf^2}{2(\cosh(sf \frac{D}{2}) - 1)} * x^2 + \frac{d_c sf^4}{24(\cosh(sf \frac{D}{2}) - 1)} * x^4 \quad (7)$$

Again y, x, sf, d_c , and D are defined as shown above.

The depth (d_c) and diameter (D) of the dimple may be measured as shown in FIG. 4.

It is understood that, based on the equations and disclosure herein, one skilled in the art would be able to derive other expressions illustrating catenary dimple profiles relating diameter, chord or surface depth, and shape factor. Therefore, the present invention is not limited to the example equations discussed above; rather, the present invention encompasses

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other expressions illustrating catenary dimple profiles relating diameter, chord or surface depth, and shape factor.

In yet another embodiment of the present invention, the mathematical equation for describing the cross-sectional profile of a dimple is expressed by the following formula:

$$y = \frac{d(\cosh(sf * x) - 1)}{\cosh(sf * r) - 1} \quad (8)$$

where: y is the vertical direction coordinate with 0 at the bottom of the dimple and positive upward (away from the center of the ball);

x is the horizontal (radial) direction coordinate, with 0 at the center of the dimple;

sf is a shape constant (also called shape factor);

d is the depth of the dimple from the phantom ball surface; and

r is the radius of the dimple.

The depth (d) and radius (r) ($r = \frac{1}{2}$ diameter (D)) of the dimple may be measured as described in U.S. Pat. No. 4,729,861 (shown in FIG. 4), the disclosure of which is incorporated by reference in its entirety. The depth (d) is measured from point J to point K on the ball phantom surface 41, and the diameter (D) is measured between the dimple edge points E and F. Although FIG. 4 is meant to depict a dimple of conventional spherical shape, the described methods for measuring dimple dimensions are also applicable to the dimples of the present invention.

Some of the differences between equations (2) and (8) include the use of a) the chordal depth (d_c) in equation (2) as opposed to the depth from phantom surface d in equation (8) and b) the diameter D in equation (2) as opposed to the radius r in equation (8). Referring once again to FIG. 4, the chordal depth (d_c) is measured from point J to the chord line 162.

In addition, another difference between equations (2) and (8) is that computed volume ratios (V_r) will be different. For example, the volume ratios according to equation (8) will always be less than those computed for dimple profiles based on equation (2). However, it will be appreciated by those of ordinary skill in the art that the differences in the computed volume ratios based on the two equations are also dependent on the manner in which volume ratio is computed. In particular, if volume ratio is calculated as the ratio of total dimple volume to a cylinder based on surface depth, then volume ratio will vary for any changes in diameter, chordal depth, and shape factor. On the other hand, if volume ratio is the ratio of dimple volume (up to the chord plane) to a cylinder based on chord depth, then the volume ratio will vary only with changes in diameter and shape factor. Regardless, the greatest differences in volume ratio when using equations (2) and (8) occur as diameter and shape factor increase and chordal depth decreases.

For the equations provided above, and more specifically equation (8), shape constant values that are larger than 1 result in dimple volume ratios greater than 0.5. Preferably, shape factors are between about 20 to about 100. FIGS. 5-9 illustrate dimple profiles for shape factors of 20, 40, 60, 80, and 100, respectively, generated using equation (8). Table 1 illustrates how the volume ratio changes for a dimple with a radius of 0.05 inches and a depth of 0.025 inches.

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TABLE 1

Shape Factor	Volume Ratio
20	0.51
40	0.55
60	0.60
80	0.64
100	0.69

As shown above, increases in shape factor result in higher volume ratios for a given dimple radius and depth.

In this regard, dimple patterns that include dimple profiles based on equation (8) may be at least partially driven by a desired percentage of dimples in the pattern that have a certain volume ratio. For example, one pattern may include about 50 percent or more dimples with a volume ratio of about 0.50 or greater. In one embodiment, about 50 percent to about 80 percent of the dimples have a volume ratio of about 0.5 to about 0.60 and about 20 percent to about 50 percent have a volume ratio of about 0.64 or greater.

In contrast, many different but related shapes of dimples can be generated by manipulating the parameters of equation (2) and other expressions illustrating catenary dimple profiles relating diameter, chord or surface depth, and shape factor. For example, FIG. 10 shows catenary dimple profiles with varying shape factors (diameter and chordal depth are held constant). Table 3 illustrates the increase in volume ratio as shape factor increases from 50 to 150. In particular, an increase in shape factor from 50 to 150 results in an increase in volume ratio of about 133 percent.

TABLE 2

Shape Factor	Diameter (in.)	Chordal Depth (in.)	Volume Ratio
50	0.15	0.006	0.63
100			0.77
150			0.84

In addition, while not exactly correlative due to the differences between equations (2) and (8), the larger diameters and shallower depth used in FIG. 10 and Table 2 appear to increase the volume ratio. For example, when applied to equation (8), a shape factor of 100, a radius of 0.05 inches, and a depth of 0.025 inches results in a volume ratio of 0.69, whereas the same shape factor with a larger diameter, but shallower dimple profile based on equation (2) results in a volume ratio of 0.77. This is an example of one of number of differences between equations (2) and (8), i.e., the volume ratios computed for dimple profiles according to equation (2) are larger than the volume ratios computed for dimple profiles according to equation (8).

FIG. 11 shows catenary dimple profiles with varying diameters (shape factor and chordal depth are held constant). Table 3 illustrates the increase in volume ratio with a corresponding increase in dimple diameter from 0.120 inches to 0.170 inches.

TABLE 3

Diameter (in.)	Shape Factor	Chordal Depth (in.)	Volume Ratio
0.120	100	0.006	0.72
0.150			0.77
0.170			0.79

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Again, when comparing this result to the results above for equation (8), a larger diameter, shallower dimple profile results in a larger volume ratio at a shape factor of 100.

In this aspect of the invention, when chordal depth is varied and shape factor and diameter is held constant (the diameter is still larger than previously used in equation (8), a larger volume ratio can be obtained when compared to the smaller, deeper dimples used above in equation (8). In particular, FIG. 12 and Table 4 illustrate that, with chordal depth ranging from 0.003 inches to 0.009 inches while the shape factor is held constant at 100 and the diameter is held constant at 0.15 inches, the volume ratio does not change, but it remains larger than the results shown in FIG. 10 and Table 1.

TABLE 4

Chordal Depth (in.)	Shape Factor	Diameter (in.)	Volume Ratio
0.003	100	0.150	0.77
0.006			0.77
0.009			0.77

Without being bound to any particular theory, it is believed that, when used with specific dimple counts, combinations of these three parameters produce optimal flight performance. In particular, specific ranges or combinations of dimple count, diameter, shape factor, and chordal depth (in accordance with equation (2)) are believed to produce optimal flight performance. For example, the number of dimples may range from about 250 to about 500. In one embodiment, the dimple count is from about 250 to about 450. In another embodiment, the dimple count is from about 250 to about 400. In still another embodiment, the number of dimples ranges from about 250 to about 350.

The diameter of the dimples may range from about 0.100 inches to about 0.225 inches. In one embodiment, the dimple diameter ranges from about 0.115 inches to about 0.200 inches. In another embodiment, the dimple diameter ranges from about 0.115 inches to about 0.185 inches. In yet another embodiment, the dimple diameter ranges from about 0.125 inches to about 0.185 inches.

As discussed briefly above, the use of a shape factor, in tandem with a cross-sectional profile based on the revolution of catenary curve according to equations (2) and (5)-(8), facilitate optimization of the flight profile of specific ball designs. As such, the shape factor may range from about 5 to about 200. In one embodiment, the shape factor ranges from about 10 to about 100. In another embodiment, the shape factor ranges from about 10 to about 75. In still another embodiment, the shape factor ranges from about 40 to about 150. In yet another embodiment, the shape factor is at least about 50.

The chordal depth of the dimple may range from about 0.002 inches to about 0.010 inches, preferably about 0.002 inches to about 0.008 inches. In one embodiment, the chordal depth is about 0.003 inches to about 0.009 inches. In another embodiment, the chordal depth is about 0.004 inches to about 0.006 inches.

It is clear from the tables above and associated figures that, when the dimple profile is based on equation (2), the volume ratio changes with changes in diameter and shape factor. In fact, as discussed previously, the volume ratio calculated for dimple profiles according to equation (2) will be larger than the volume ratio calculated for dimple profiles according to equation (8). In particular, shallow, large diameter dimples with profiles based on equation (2) results in a larger volume

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ratio as compared with dimples having more substantive depth and smaller diameters such as those based on equation (8) above.

Dimple profiles based on equation (2) with dimple diameters between about 0.100 inches and about 0.225 inches (or any range therebetween) and chordal depths between about 0.002 inches to about 0.008 inches (or any range therebetween) preferably have volume ratios at least about 0.60 or greater. In one embodiment, the volume ratio is about 0.63 or greater. In another embodiment, the volume ratio is about 0.070 or greater. In still another embodiment, the volume ratio is about 0.72 or greater. For example, the volume ratio may be between about 0.63 to about 0.84.

In one embodiment, at least 50 percent of the dimples on the golf ball have a dimple profile based on equation (2). In another embodiment, at least about 80 percent of the dimples are based on equation (2). In still another embodiment, at least about 90 percent of the dimples are based on equation (2). In yet another embodiment, 100 percent of the dimples have a dimple profile according to equation (2).

Within these constraints, a portion of this percentage may be based on equation (2) with a fixed chordal depth and shape factor and varying diameters. For example, about 50 percent or more of the dimples having a dimple profile based on equation (2) may have a fixed chordal depth and shape factor and a varying diameter. In one embodiment, the diameter may range from about 0.100 to about 0.225, preferably about 0.115 inches to about 0.200 inches, more preferably about 0.115 inches to about 0.185 inches, and even more preferably about 0.125 inches to about 0.185 inches while the shape factor is constant and from about 5 to about 200, preferably about 10 to about 100, more preferably about 10 to about 75 and the chordal depth is constant and from about 0.002 inches to about 0.008 inches, preferably about 0.003 inches to about 0.006 inches, and more preferably about 0.004 inches to about 0.006 inches. The remaining dimples within the percentage of the dimples on the ball having a profile according to equation (2) may have varying chordal depth and/or shape factor within these ranges and a fixed diameter within the range of 0.100 inches to about 0.225 inches, preferably about 0.115 inches to about 0.200 inches, more preferably about 0.115 inches to about 0.185 inches, and even more preferably about 0.125 inches to about 0.185 inches.

One dimple pattern according to the invention has about 50 percent to about 100 percent of its dimples based on equation (2) with a varying diameter within the range of 0.125 inches to about 0.185 inches and a fixed chordal depth of about 0.004 inches to about 0.006 inches and a fixed shape factor between about 10 to about 75. If less than 100 percent of the dimples are based on equation (2), the remainder of the dimples may have cross-sectional profiles based on parabolic curves, ellipses, semi-spherical curves, saucer-shapes, sine curves, truncated cones, flattened trapezoids, or catenary curves according to equation (2) and/or equations (5)-(8).

For example, dimple patterns according to the present invention may be formed using a combination of equations (2) and (8). For example, in one embodiment, at least a portion of the dimples have a profile based on equation (2) and the remaining portion have dimple profiles based equation (8). In this aspect, about 5 percent to about 40 percent have dimple profiles based on equation (8) and about 60 percent to about 95 percent have dimple profiles based on equation (2). In another embodiment, about 5 percent to about 20 percent have dimple profiles based on equation (8) and about 80 percent to about 95 percent have dimple profiles based on equation (2).

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The portion of the dimples having profiles based on equation (8) has a fixed radius and surface depth of 0.05 to about 0.09 inches and 0.005 to about 0.025 inches, respectively, with varying shape factors. For example, the shape factor may vary from 20 to 100. In one embodiment, the shape factor is at least about 40, but may vary up to 100. In fact, within the percentage of dimples having profiles based on equation (8), preferably about 50 percent or more have a shape factor of 50 or greater. While two or more shape factors may be used for dimples on a golf ball, it is preferred that the differences between the shape factors be relatively similar in order to achieve optimum ball flight performance that corresponds to a particular ball construction and player swing speed. In particular, a plurality of shape factors used to define dimples having catenary curves preferably do not differ by more than 30, and even more preferably do not differ by more than 15.

In this same scenario, the portion of the dimples based on equation (2) may have varying diameter, chordal depth, and shape factor. For example, within the percentage of dimples having a profile based on equation (2), at least 50 percent may have a fixed chordal depth and shape factor with a diameter ranging from about 0.100 to about 0.225, preferably about 0.115 inches to about 0.200 inches, more preferably about 0.115 inches to about 0.185 inches, and even more preferably about 0.125 inches to about 0.185 inches, while the remaining portion of these dimples are a mix of dimple profiles based on equation (2) holding diameter constant, while varying either the shape factor or chordal depth. In one embodiment, about 50 percent to about 80 percent of the dimples having a dimple profile based on equation (2) have a fixed chordal depth and shape factor with varying diameter and about 20 percent to about 50 percent are a mix of varying chordal depth with fixed diameter and fixed shape factor and varying shape factor with fixed diameter and chordal depth.

The use of a dimple shape factor in the catenary curve profiles of the present invention helps to yield particular optimal flight performance for specific swing speed categories. Again, the advantageous feature of shape factor is that dimple location need not be manipulated for each swing speed; only the dimple shape will be altered. Thus, a "family" of golf balls may have a similar general appearance although the dimple shape for at least a portion of the dimples on the ball is altered to optimize flight characteristics for particular swing speeds. Table 5 identifies certain beneficial shape factors for varying swing speeds, i.e., from 155-175 mph, from 140 to 155 mph, and from 125 to 140 mph, cover hardness, and ball compression.

TABLE 5

Ball Design	Dimple Shape Factor	Ball Speed from driver (mph)	Cover Hardness (Shore D)	Ball Compression (Atti)
1	80	155-175	45-55	60-75
2	90	155-175	45-55	75-90
3	100	155-175	45-55	90-105
4	70	155-175	55-65	60-75
5	80	155-175	55-65	75-90
6	90	155-175	55-65	90-105
7	55	155-175	65-75	60-75
8	65	155-175	65-75	75-90
9	75	155-175	65-75	90-105
10	65	140-155	45-55	60-75
11	75	140-155	45-55	75-90
12	85	140-155	45-55	90-105
13	55	140-155	55-65	60-75
14	65	140-155	55-65	75-90
15	75	140-155	55-65	90-105
16	40	140-155	65-75	60-75

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TABLE 5-continued

Ball Design	Dimple Shape Factor	Ball Speed from driver (mph)	Cover Hardness (Shore D)	Ball Compression (Atti)
17	50	140-155	65-75	75-90
18	60	140-155	65-75	90-105
19	50	125-140	45-55	60-75
20	60	125-140	45-55	75-90
21	70	125-140	45-55	90-105
22	40	125-140	55-65	60-75
23	50	125-140	55-65	75-90
24	60	125-140	55-65	90-105
25	25	125-140	65-75	60-75
26	35	125-140	65-75	75-90
27	45	125-140	65-75	90-105

To illustrate the selection of shape factors in dimple design from Table 5, the preferred dimple shape factor for a ball having a cover hardness of about 45 to about 55 Shore D and a ball compression of about 60 to about 75 Atti for a player with a ball speed from the driver between about 140 and about 155 mph would be about 65. Likewise, the preferred shape factor for the same ball construction, but for a player having a ball speed from the driver of between about 155 mph and about 175 mph would be about 80. As mentioned above, these preferred shape factors may be adjusted upwards or downwards by 20, 10, or 5 to arrive at a further customized ball design.

Table 5 shows that as the spin rate and ball speed off the driver increase, the shape factor should also increase to provide optimal aerodynamic performance, e.g., increased flight distance. While the shape factors listed above illustrate preferred embodiments for varying ball constructions and ball speeds, the shape factors listed above for each example may be varied without departing from the spirit and scope of the present invention. For example, in one embodiment, the shape factors listed for each example above may be adjusted upwards or downwards by 20 to arrive at a further customized ball design. More preferably, the shape factors may be adjusted upwards or downwards by 10, and even more preferably it may be adjusted by 5.

Thus, shape factors may be selected for a particular ball construction that result in a ball designed to work well with a wide variety of player swing speeds. For instance, in one embodiment of the present invention, a shape factor between about 65 and about 100 would be suitable for a ball with a cover hardness between about 45 and about 55 shore D.

As such, not only do the preferred ranges of dimple radius and/or diameter, depth, and shape factor discussed above with respect to equations (2) and (8) factor into the design of a dimple profile and overall dimple pattern, the player swing speed will also likely play a role. In this regard, the range of shape factors for dimple profiles based on equations (2) or (8) may be adjusted to cater to a certain player swing speed. For example, while a preferred shape factor range is from about 10 to about 75, this may be adjusted depending on the targeted player swing speed and ball construction.

Dimple Patterns

Dimple patterns that provide a high percentage of surface coverage are preferred, and are well known in the art. For example, U.S. Pat. Nos. 5,562,552, 5,575,477, 5,957,787, 5,249,804, and 4,925,193 disclose geometric patterns for positioning dimples on a golf ball. In one embodiment of the present invention, the dimple pattern is at least partially defined by phyllotaxis-based patterns, such as those

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described in copending U.S. Pat. No. 6,338,684, the entire disclosure of which is incorporated by reference in its entirety.

In one embodiment, the selected dimple pattern provides greater than about 50 percent surface coverage. In another embodiment, about 70 percent or more of the golf ball surface is covered by dimples. In yet another embodiment, about 80 percent or more of the golf ball surface is covered by dimples. In still another embodiment, about 90 percent or more of the golf ball surface is covered by dimples. Various patterns with varying levels of coverage are discussed below. Any of these patterns or modification to these patterns are contemplated for use in accordance with the present invention.

FIGS. 13 and 14 show a golf ball 10 with a plurality of dimples 11 on the outer surface that are formed into a dimple pattern having two sizes of dimples. The first set of dimples A have diameters of about 0.14 inches and form the outer triangle 12 of the icosahedron dimple pattern. The second set of dimples B have diameters of about 0.16 inches and form the inner triangle 13 and the center dimple 14. The dimples 11 cover less than 80 percent of the outer surface of the golf ball and there is a significant number of large spaces 15 between adjacent dimples, i.e., spaces that could hold a dimple of 0.03 inches diameter or greater.

FIGS. 15 and 16 show a golf ball 20 according to the first dimple pattern embodiment of the present invention with a plurality of dimples 21 in an icosahedron pattern. In an icosahedron pattern, there are twenty triangular regions that are generally formed from the dimples. The icosahedron pattern has five triangles formed at both the top and bottom of the ball, each of which shares the pole dimple as a point. There are also ten triangles that extend around the middle of the ball.

In this first dimple pattern embodiment, there are five different sized dimples A-E, wherein dimples E (D_E) are greater than dimples D (D_D), which are greater than dimples C (D_C), which are greater than dimples B (D_B), which are greater than dimples A (D_A); $D_E > D_D > D_C > D_B > D_A$. Dimple minimum sizes according to this embodiment are set forth in Table 6 below:

TABLE 6

Dimple Sizes for Suitable Dimple Pattern	
Dimple	Percent of Ball Diameter
A	6.55
B	8.33
C	9.52
D	10.12
E	10.71

The dimples of this embodiment are formed in large triangles 22 and small triangles 23. The dimples along the sides of the large triangle 22 increase in diameter toward the midpoint 24 of the sides. The largest dimple along the sides, D_E , is located at the midpoint 24 of each side of the large triangle 22, and the smallest dimples, D_A , are located at the triangle points 25. In this embodiment, each dimple along the sides is larger than the adjacent dimple toward the triangle point.

FIGS. 17-20 illustrate another suitable dimple pattern contemplated for use on the golf ball of the present invention. In this embodiment, there are again five different sized dimples A-E, wherein dimples E (D_E) are greater than dimples D (D_D), which are greater than dimples C (D_C), which are greater than dimples B (D_B), which are greater than dimples A (D_A); $D_E > D_D > D_C > D_B > D_A$. Dimple minimum sizes according to this embodiment are set forth in Table 7 below:

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TABLE 7

Dimple Sizes for Suitable Dimple Pattern	
Dimple	Percent of Ball Diameter
A	6.55
B	8.93
C	9.23
D	9.52
E	10.12

In this dimple pattern, the dimples are again formed in large triangles 22 and small triangles 23 as shown in FIG. 19. The dimples along the sides of the large triangle 22 increase in diameter toward the midpoint 24 of the sides. The largest dimple along the sides, D_D , is located at the midpoint 24 of each side of the large triangle 22, and the smallest dimples, D_A , are located at the triangle points 25. In this embodiment, each dimple along the sides is larger than the adjacent dimple toward the triangle point, i.e., $D_B > D_A$ and $D_D > D_B$.

Another suitable dimple pattern embodiment is illustrated in FIGS. 21-22, wherein the golf ball has an octahedral dimple pattern. In an octahedral dimple pattern, there are eight spherical triangular regions 30 that form the ball. In this dimple pattern, there are six different sized dimples A-F, wherein dimples F (D_F) are greater than dimples E (D_E), which are greater than dimples D (D_D), which are greater than dimples C (D_C), which are greater than dimples B (D_B), which are greater than dimples A (D_A); $D_F > D_E > D_D > D_C > D_B > D_A$. Dimple minimum sizes according to this embodiment are set forth in Table 8 below:

TABLE 8

Dimple Sizes for Suitable Dimple Pattern	
Dimple	Percentage of Ball Diameter
A	5.36
B	6.55
C	8.33
D	9.83
E	9.52
F	10.12

In this dimple pattern embodiment, the dimples are formed in large triangles 31, small triangles 32 and smallest triangles 33. Each dimple along the sides of the large triangle 31 is equal to or larger than the adjacent dimple from the point 34 to the midpoint 35 of the triangle 31. The dimples at the midpoint 35 of the side, D_E , are the largest dimples along the side and the dimples at the points 34 of the triangle, D_A , are the smallest. In addition, each dimple along the sides of the small triangle 32 is also equal to or larger than the adjacent dimple from the point 36 to the midpoint 37 of the triangle 32. The dimple at the midpoint 37 of the side, D_F , is the largest dimple along the side and the dimples at the points 36 of the triangle, D_C , are the smallest.

Dimple Packing

In one embodiment, the golf balls of the invention include an icosahedron dimple pattern, wherein each of the sides of the large triangles is formed from an odd number of dimples and each of the side of the small triangles are formed with an even number of dimples.

For example, in the icosahedron pattern shown in FIGS. 15-16 and 17-20, there are seven dimples along each of the

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sides of the large triangle 22 and four dimples along each of the sides of the small triangle 23. Thus, the large triangle 22 has nine more dimples than the small triangle 23, which creates hexagonal packing 26, i.e., each dimple is surrounded by six other dimples for most of the dimples on the ball. For example, the center dimple, D_E , is surrounded by six dimples slightly smaller, D_D . In one embodiment, at least 75 percent of the dimples have 6 adjacent dimples. In another embodiment, only the dimples forming the points of the large triangle 25, D_A , do not have hexagonal packing. Since D_A are smaller than the adjacent dimples, the gaps between adjacent dimples is surprisingly small when compared to the golf ball shown in FIG. 15.

The golf ball 20 has a greater dispersion of the largest dimples. For example, in FIG. 15, there are four of the largest diameter dimples, D_E , located in the center of the triangles and at the mid-points of the triangle sides. Thus, there are no two adjacent dimples of the largest diameter. This improves dimple packing and aerodynamic uniformity. Similarly, in FIG. 17, there is only one largest diameter dimple, D_E , which is located in the center of the triangles. Even the next to the largest dimples, D_D , are dispersed at the mid-points of the large triangles such that there are no two adjacent dimples of the two largest diameters, except where extra dimples have been added along the equator.

In the last example dimple pattern discussed above, i.e., FIGS. 21-22, each of the sides of the large triangle 31 has an even number of dimples, each of the sides of the small triangle 32 has an odd number of dimples and each of the sides of the smallest triangle 33 has an even number of dimples. There are ten dimples along the sides of the large triangles 31, seven dimples along the sides of the small triangles 32, and four dimples along the sides of the smallest triangles 33. Thus, the large triangle 31 has nine more dimples than the small triangle 32 and the small triangle 32 has nine more dimples than the smallest triangle 33. This creates the hexagonal packing for all of the dimples inside of the large triangles 31.

As used herein, adjacent dimples can be considered as any two dimples where the two tangent lines from the first dimple that intersect the center of the second dimple do not intersect any other dimple. In one embodiment, less than 30 percent of the gaps between adjacent dimples is greater than 0.01 inches. In another embodiment, less than 15 percent of the gaps between adjacent dimples is greater than 0.01 inches.

As discussed above, one embodiment of the present invention contemplates dimple coverage of greater than about 80 percent. For example, the percentages of surface area covered by dimples in the embodiments shown in FIGS. 15-16 and 17-20 are about 85.7 percent and 82 percent, respectively whereas the ball shown in FIG. 14 has less than 80 percent of its surface covered by dimples. The percentage of surface area covered by dimples as shown in FIGS. 21-22 is also about 82 percent, whereas prior art octahedral balls have less than 77 percent of their surface covered by dimples, and most have less than 60 percent. Thus, there is a significant increase in surface area contemplated for the golf balls of the present invention as compared to prior art golf balls.

Parting Line

A parting line, or annular region, about the equator of a golf ball has been found to separate the flow profile of the air into two distinct halves while the golf ball is in flight and reduce the aerodynamic force associated with pressure recovery, thus improving flight distance and roll. The parting line must coincide with the axis of ball rotation. It is possible to manufacture a golf ball without parting line, however, most balls have one for ease of manufacturing, e.g., buffing of the golf

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balls after molding, and many players prefer to have a parting line to use as an alignment aid for putting.

In one embodiment of the present invention, the golf balls include a dimple pattern containing at least one parting line, or annular region. In another embodiment, there is no parting line that does not intersect any dimples, as illustrated in the golf ball shown in FIG. 15. While this increases the percentage of the outer surface that is covered by dimples, the lack of the parting line may make manufacturing more difficult.

In yet another embodiment, the dimple pattern is such that any dimples adjacent to the parting line are aligned and positioned to overlap across the parting line. In essence, this creates a staggered wave parting line. Examples of such dimple patterns are described in U.S. Pat. Nos. 7,258,632 and 6,969,327 and U.S. Patent Publication No. 2006/0025245, the disclosures of which are incorporated by reference herein.

In yet another embodiment, the parting line(s) may include regions of no dimples or regions of shallow dimples. For example, most icosahedron patterns generally have modified triangles around the mid-section to create a parting line that does not intersect any dimples. Referring specifically to FIG. 20, the golf ball in this embodiment has a modified icosahedron pattern to create the parting line 27, which is accomplished by inserting an extra row of dimples. In the triangular section identified with lettered dimples, there is an extra row 28 of D-C-C-D dimples added below the parting line 27. Thus, the modified icosahedron pattern in this embodiment has thirty more dimples than the unmodified icosahedron pattern in the embodiment shown in FIGS. 15-16.

In another embodiment, there are more than two parting lines that do not intersect any dimples. For example, the octahedral golf ball shown in FIGS. 21-22 contains three parting lines 38 that do not intersect any dimples. This decreases the percentage of the outer surface as compared to the first embodiment, but increases the symmetry of the dimple pattern. In another embodiment, the golf balls according to the present invention may have the dimples arranged so that there are less than four parting lines that do not intersect any dimples.

Aerodynamic Performance

As discussed generally in the background section, dimples play a key role in the lift and drag on a golf ball. The lift and drag forces are computed as follows:

$$F_{lift}=0.5 \rho C_l A V^2 \quad (9)$$

$$F_{drag}=0.5 \rho C_d A V^2 \quad (10)$$

where: ρ =air density

C_l =lift coefficient

C_d =drag coefficient

A =ball area= πr^2 (where r =ball radius), and

V =ball velocity

Lift and drag coefficients are dependent on air density, air viscosity, ball speed, and spin rate and the influence of all of these parameters may be captured by two dimensionless parameters, i.e., Reynolds Number (N_{Re}) and Spin Ratio (SR). Spin Ratio is the rotational surface speed of the ball divided by ball velocity. Reynolds Number quantifies the ratio of inertial to viscous forces acting on the golf ball moving through the air. SR and N_{Re} are calculated in equations (11) and (12) below:

$$SR=\omega(D/2)/V \quad (11)$$

$$N_{Re}=DV\rho/\mu \quad (12)$$

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where ω =ball rotation rate (radians/s) ($2\pi(\text{RPS})$)

RPS=ball rotation rate (revolution/s)

V=ball velocity (ft/s)

D=ball diameter (ft)

ρ =air density (slugs/ft³)

μ =absolute viscosity of air (lb/ft-s)

There is a number of suitable methods for determining the lift and drag coefficients for a given range of SR and N_{Re} , which include the use of indoor test ranges with ballistic screen technology. U.S. Pat. No. 5,682,230, the entire disclosure of which is incorporated by reference herein, teaches the use of a series of ballistic screens to acquire lift and drag coefficients. U.S. Pat. Nos. 6,186,002 and 6,285,445, also incorporated in their entirety by reference herein, disclose methods for determining lift and drag coefficients for a given range of velocities and spin rates using an indoor test range, wherein the values for C_L and C_D are related to SR and N_{Re} for each shot. One skilled in the art of golf ball aerodynamics testing could readily determine the lift and drag coefficients through the use of an indoor test range.

For a golf ball of any diameter and weight, increased distance is obtained when the lift force, F_{lift} , on the ball is greater than the weight of the ball but preferably less than three times its weight. This may be expressed as:

$$W_{ball} \leq F_{lift} \leq 3W_{ball}$$

The preferred lift coefficient range which ensures maximum flight distance is thus:

$$\frac{2W_{ball}}{\pi^2 \rho V^2} \leq C_L \leq \frac{6W_{ball}}{\pi^2 \rho V^2}$$

The lift coefficients required to increase flight distance for golfers with different ball launch speeds may be computed using the formula provided above. Table 9 provides several examples of the preferred range for lift coefficients for alternative launch speeds, ball size, and weight:

TABLE 9

PREFERRED RANGES FOR LIFT COEFFICIENT FOR A GIVEN BALL DIAMETER, WEIGHT, AND LAUNCH VELOCITY FOR A GOLF BALL ROTATING AT 3000 RPM						
Preferred Minimum C_L	Preferred Maximum C_L	Ball Diameter (in.)	Ball Weight (oz.)	Ball Velocity (ft/s)	Reyn- olds Number	Spin Ratio
0.09	0.27	1.75	1.8	250	232008	0.092
0.08	0.24	1.75	1.62	250	232008	0.092
0.07	0.21	1.75	1.4	250	232008	0.092
0.10	0.29	1.68	1.8	250	222727	0.088
0.09	0.27	1.68	1.62	250	222727	0.088
0.08	0.23	1.68	1.4	250	222727	0.088
0.12	0.37	1.5	1.8	250	198864	0.079
0.11	0.33	1.5	1.62	250	198864	0.079
0.10	0.29	1.5	1.4	250	198864	0.079
0.14	0.42	1.75	1.8	200	185606	0.115
0.13	0.38	1.75	1.62	200	185606	0.115
0.11	0.33	1.75	1.4	200	185606	0.115
0.15	0.46	1.68	1.8	200	178182	0.110
0.14	0.41	1.68	1.62	200	178182	0.110
0.12	0.36	1.68	1.4	200	178182	0.110

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TABLE 9-continued

PREFERRED RANGES FOR LIFT COEFFICIENT FOR A GIVEN BALL DIAMETER, WEIGHT, AND LAUNCH VELOCITY FOR A GOLF BALL ROTATING AT 3000 RPM						
Preferred Minimum C_L	Preferred Maximum C_L	Ball Diameter (in.)	Ball Weight (oz.)	Ball Velocity (ft/s)	Reyn- olds Number	Spin Ratio
0.19	0.58	1.5	1.8	200	159091	0.098
0.17	0.52	1.5	1.62	200	159091	0.098
0.15	0.45	1.5	1.4	200	159091	0.098

Because of the key role a dimple profile plays in lift and drag on a golf ball, once a dimple pattern is selected for the golf ball, the shape factor used in the catenary curve equations may be adjusted to achieve the desired lift coefficient. Effective ways of arriving at the optimal shape factor(s) include wind tunnel testing or using a light gate test range to empirically determine the catenary shape factor that provides the desired lift coefficient at the desired launch velocity. Preferably, the measurement of lift coefficient is performed with the golf ball rotating at typical driver rotation speeds. A preferred spin rate for performing the lift and drag tests is 3,000 rpm.

In addition to selecting particular dimple profiles based on catenary curves, improved flight distance may also be achieved by selecting the dimple pattern and dimple profiles so that specific magnitude and direction criteria are satisfied. In particular, two parameters that account for both lift and drag simultaneously, i.e., 1) the magnitude of aerodynamic force (C_{mag}) and 2) the direction of the aerodynamic force (Angle), are linearly related to the lift and drag coefficients. Therefore, the magnitude and angle of the aerodynamic coefficients may be used as an additional tool to achieve the desired aerodynamic performance of the ball. The magnitude and the angle of the aerodynamic coefficients are defined in equations (13) and (14) below:

$$C_{mag} = \sqrt{(C_L^2 + C_D^2)} \quad (13)$$

$$\text{Angle} = \tan^{-1}(C_L/C_D) \quad (14)$$

Table 10 illustrates the aerodynamic criteria for a golf ball of the present invention that results in increased flight distances. The criteria are specified as low, median, and high C_{mag} and Angle for eight specific combinations of SR and N_{Re} . Golf balls with C_{mag} and Angle values between the low and the high number are preferred. More preferably, the golf balls of the invention have C_{mag} and Angle values between the low and the median numbers delineated in Table 10. The C_{mag} values delineated in Table 10 are intended for golf balls that conform to USGA size and weight regulations. The size and weight of the golf balls used with the aerodynamic criteria of Table 10 are 1.68 inches and 1.62 ounces, respectively.

TABLE 10

Aerodynamic Characteristics Ball Diameter = 1.68 inches, Ball Weight = 1.62 ounces							
N_{Re}	SR	Magnitude ¹			Angle ² (°)		
		Low	Median	High	Low	Median	High
230000	0.085	0.24	0.265	0.27	31	33	35
207000	0.095	0.25	0.271	0.28	34	36	38
184000	0.106	0.26	0.280	0.29	35	38	39
161000	0.122	0.27	0.291	0.30	37	40	42
138000	0.142	0.29	0.311	0.32	38	41	43
115000	0.170	0.32	0.344	0.35	40	42	44

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TABLE 10-continued

Aerodynamic Characteristics Ball Diameter = 1.68 inches, Ball Weight = 1.62 ounces							
N_{Re}	SR	Magnitude ¹			Angle ² (°)		
		Low	Median	High	Low	Median	High
92000	0.213	0.36	0.390	0.40	41	43	45
69000	0.284	0.40	0.440	0.45	40	42	44

¹As defined by equation (13)²As defined by equation (14)

To ensure consistent flight performance regardless of ball orientation, the percent deviation of C_{mag} for each of the SR and N_{Re} combinations listed in Table 10 plays an important role. The percent deviation of C_{mag} may be calculated in accordance with equation (15), wherein the ratio of the absolute value of the difference between the C_{mag} for two orientations to the average of the C_{mag} for the two orientations is multiplied by 100.

$$\text{Percent deviation } C_{mag} = |C_{mag1} - C_{mag2}| / ((C_{mag1} + C_{mag2}) / 2) * 100 \quad (15)$$

where $C_{mag1} = C_{mag}$ for orientation 1

$C_{mag2} = C_{mag}$ for orientation 2

In one embodiment, the percent deviation is about 6 percent or less. In another embodiment, the deviation of C_{mag} is about 3 percent or less. To achieve the consistent flight performance, the percent deviation criteria of equation (15) is preferably satisfied for each of the eight C_{mag} values associated with the eight SR and N_{Re} values contained in Table 10.

Aerodynamic asymmetry may arise from parting lines that are inherent in the dimple arrangement or from parting lines associated with the manufacturing process. The percent C_{mag} deviation should be obtained using C_{mag} values measured with the axis of rotation normal to the parting line, commonly referred to as a poles horizontal, PH, orientation and C_{mag} values measured in an orientation orthogonal to PH, commonly referred to as a pole over pole, PP orientation. The maximum aerodynamic asymmetry is generally measured between the PP and PH orientation.

One of ordinary skill in the art would be aware, however, that the percent deviation of C_{mag} as outlined above applies to PH and PP, as well as any other two orientations. For example, if a particular dimple pattern is used having a great circle of shallow dimples, which will be described in greater detail below, different orientations should be measured. The axis of

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rotation to be used for measurement of symmetry in the above example scenario would be normal to the plane described by the great circle and coincident to the plane of the great circle.

It has also been discovered that the C_{mag} and Angle criteria delineated in Table 10 for golf balls with a nominal diameter of 1.68 and a nominal weight of 1.62 ounces may be advantageously scaled to obtain the similar optimized criteria for golf balls of any size and weight. The aerodynamic criteria of Table 10 may be adjusted to obtain the C_{mag} and angle for golf balls of any size and weight in accordance with equations (16) and (17).

$$C_{mag(ball)} = C_{mag(Table\ 10)} \sqrt{\left(\frac{\sin(\text{Angle}_{(Table\ 10)})}{\sin(\text{Angle}_{(ball)})} \right)^2 \left(\frac{W_{ball}}{W_{Table\ 10}} \right)^2} \quad (16)$$

$$\text{Angle}_{(ball)} = \tan^{-1} \left(\tan(\text{Angle}_{(Table\ 10)}) \left(\frac{W_{ball}}{W_{Table\ 10}} \right)^{1/2} \right) \quad (17)$$

For example, Table 11 illustrates aerodynamic criteria for balls with a diameter of 1.60 inches and a weight of 1.7 ounces as calculated using Table 10, ball diameter, ball weight, and equations (13) and (14).

TABLE 11

Aerodynamic Characteristics Ball Diameter = 1.60 inches, Ball Weight = 1.70 ounces							
N_{Re}	SR	Magnitude ¹			Angle ² (°)		
		Low	Median	High	Low	Median	High
230000	0.085	0.24	0.265	0.27	31	33	35
207000	0.095	0.262	0.287	0.297	38	40	42
184000	0.106	0.271	0.297	0.308	39	42	44
161000	0.122	0.83	0.311	0.322	42	44	46
138000	0.142	0.304	0.333	0.346	43	45	47
115000	0.170	0.337	0.370	0.383	44	46	49
92000	0.213	0.382	0.420	0.435	45	47	50
69000	0.284	0.430	0.473	0.489	44	47	49

¹As defined by equation (13)²As defined by equation (14)

Table 12 shows lift and drag coefficients (C_L , C_D), as well as C_{mag} and Angle, for a golf ball having a nominal diameter of 1.68 inches and a nominal weight of 1.61 ounces, with an icosahedron pattern with 392 dimples and two dimple diameters, of which the dimple pattern will be described in more detail below. The percent deviation in C_{mag} for PP and PH ball orientations are also shown over the range of N_{Re} and SR. The deviation in C_{mag} for the two orientations over the entire range is less than about 3 percent.

TABLE 12

Aerodynamic Characteristics Ball Diameter = 1.68 inches, Ball Weight = 1.61 ounces										
N_{Re}	SR	PP Orientation				PH Orientation				%
		C_L	C_D	C_{mag}^1	Angle ²	C_L	C_D	C_{mag}^1	Angle ²	
230000	0.085	0.144	0.219	0.262	33.4	0.138	0.217	0.257	32.6	1.9
207000	0.095	0.159	0.216	0.268	36.3	0.154	0.214	0.264	35.7	1.8
184000	0.106	0.169	0.220	0.277	37.5	0.166	0.216	0.272	37.5	1.8
161000	0.122	0.185	0.221	0.288	39.8	0.181	0.221	0.286	39.4	0.9
138000	0.142	0.202	0.232	0.308	41.1	0.199	0.233	0.306	40.5	0.5

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TABLE 12-continued

Aerodynamic Characteristics Ball Diameter = 1.68 inches, Ball Weight = 1.61 ounces										
N_{Re}	SR	PP Orientation				PH Orientation				% Dev C_{mag}
		C_L	C_D	C_{mag}^1	Angle ²	C_L	C_D	C_{mag}^1	Angle ²	
115000	0.170	0.229	0.252	0.341	42.2	0.228	0.252	0.340	42.2	0.2
92000	0.213	0.264	0.281	0.386	43.2	0.270	0.285	0.393	43.5	1.8
69000	0.284	0.278	0.305	0.413	42.3	0.290	0.309	0.423	43.2	2.5
SUM		2.543				SUM 2.541				

¹As defined by equation (16)²As defined by equation (17)

Table 13 shows lift and drag coefficients (C_L , C_D), as well as C_{mag} and Angle for a prior golf ball having a nominal diameter of 1.68 inches and a nominal weight of 1.61 ounces. The percent deviation in C_{mag} for PP and PH ball orientations are also shown over the range of N_{Re} and SR. The deviation in

C_{mag} for the two orientations is greater than about 3 percent over the entire range, greater than about 6 percent for N_{Re} of 161000, 138000, 115000, and 92000, and exceeds 10 percent at a N_{Re} of 69000.

TABLE 13

Aerodynamic Characteristics For Prior Art Golf Ball Ball Diameter = 1.68 inches, Ball Weight = 1.61 ounces										
N_{Re}	SR	PP Orientation				PH Orientation				% Dev C_{mag}
		C_L	C_D	C_{mag}^1	Angle ²	C_L	C_D	C_{mag}^1	Angle ²	
230000	0.085	0.151	0.222	0.269	34.3	0.138	0.219	0.259	32.3	3.6
207000	0.095	0.160	0.223	0.274	35.6	0.145	0.219	0.263	33.4	4.1
184000	0.106	0.172	0.227	0.285	37.2	0.154	0.221	0.269	34.8	5.6
161000	0.122	0.188	0.233	0.299	38.9	0.166	0.225	0.279	36.5	6.9
138000	0.142	0.209	0.245	0.322	40.5	0.184	0.231	0.295	38.5	8.7
115000	0.170	0.242	0.269	0.361	42.0	0.213	0.249	0.328	40.5	9.7
92000	0.213	0.280	0.309	0.417	42.2	0.253	0.283	0.380	41.8	9.5
69000	0.284	0.270	0.308	0.409	41.2	0.308	0.337	0.457	42.5	10.9
SUM		2.637				SUM 2.531				

¹As defined by equation (16)²As defined by equation (17)

Table 14 illustrates the flight performance of a golf ball of the present invention having a nominal diameter of 1.68 inches and weight of 1.61 ounces, compared to a prior art golf ball having similar diameter and weight. Each prior art ball is compared to a golf ball of the present invention at the same speed, angle, and back spin.

TABLE 14

Ball Flight Performance, Invention vs. Prior Art Golf Ball Ball Diameter = 1.68 inches, Ball Weight = 1.61 ounces							
	Ball Orientation	Speed (mph)	Angle	Rotation Rate	Distance (yds)	Time (s)	Impact Angle
				(rpm)			
Prior Art	PP	168.4	8.0	3500	267.2	7.06	41.4
	PH	168.4	8.0	3500	271.0	6.77	36.2
Invention	PP	168.4	8.0	3500	276.7	7.14	39.9
	PH	168.4	8.0	3500	277.6	7.14	39.2
Prior Art	PP	145.4	8.0	3000	220.8	5.59	31.3
	PH	145.4	8.0	3000	216.9	5.18	25.4
Invention	PP	145.4	8.0	3000	226.5	5.61	29.3
	PH	145.4	8.0	3000	226.5	5.60	28.7

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Table 14 shows an improvement in flight distance for a golf ball of the present invention of between about 6 to about 10 yards over a similar size and weight prior art golf ball. Table 14 also shows that the flight distance of prior art golf balls is dependent on the orientation when struck, i.e., a deviation between a PP and PH orientation results in about 4 yards distance between the two orientations. In contrast, golf balls of the present invention exhibit less than about 1 yard variation in flight distance due to orientation. Additionally, prior art golf balls exhibit large variations in the angle of ball impact with the ground at the end of flight, i.e., about 5°, for the two orientations, while golf balls of the present invention have a variation in impact angles for the two orientations of less than about 1°. A large variation in impact angle typically leads to significantly different amounts of roll when the ball strikes the ground.

The advantageously consistent flight performance of a golf ball of the present invention, i.e., the less variation in flight distance and impact angle, results in more accurate play and potentially yields lower golf scores. FIGS. 23 and 24 illustrate the magnitude of the aerodynamic coefficients and the angle of aerodynamic force plotted versus N_{Re} for a golf ball of the present invention and a prior art golf ball, each having a diameter of about 1.68 inches and a weight of about 1.61 ounces with a fixed spin rate of 3000 rpm. As shown in FIG. 23, the magnitude of the aerodynamic coefficient is substantially lower and more consistent between orientations for a golf ball of the present invention as compared to a prior art golf ball throughout the range of N_{Re} tested. FIG. 24 illustrates that the angle of the aerodynamic force is more consistent for a golf ball of the present invention as compared to a prior art golf ball.

Aerodynamic Symmetry

To create a ball that adheres to the Rules of Golf, as approved by the United States Golf Association, the ball must not be designed, manufactured or intentionally modified to have properties that differ from those of a spherically symmetrical ball. Aerodynamic symmetry allows the ball to fly with little variation no matter how the golf ball is placed on the tee or ground.

As such, the dimple patterns discussed above are preferably selected and/or designed to cover the maximum surface area of the golf ball without detrimentally affecting the aerodynamic symmetry of the golf ball. A representative coordinate system used to model some of the dimple patterns discussed above is shown in FIG. 25. The XY plane is the equator of the ball while the Z direction goes through the pole of the ball. Preferably, the dimple pattern is generated from the equator of the golf ball, the XY plane, to the pole of the golf ball, the Z direction.

As discussed above, golf balls containing dimple patterns having a parting line about the equator may result in orientation specific flight characteristics. As mentioned above, the parting lines are desired by manufacturers for ease of production, as well as by many golfers for lining up a shot for putting or off the tee. It has now been discovered that selective design of golf balls with dimple patterns including a parting line meeting the aerodynamic criteria set forth in Table 7 result in flight distances far improved over prior art. Geometrically, these parting lines must be orthogonal with the axis of rotation. However, in one embodiment of the present invention, there may be a plurality of parting lines with multiple orientations.

Another way of achieving aerodynamic symmetry or correction for asymmetrical orientation is to use a dimple pattern that congregates a certain amount of relatively shallow dimples about the poles of the golf ball. In this regard,

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dimples having profiles based on equation (2) using the preferred ranges of chordal depth, diameter, and shape factor are believed to accomplish aerodynamic symmetry. In addition, it is contemplated that dimple profiles based on equation (2) and having chordal depths between about 0.002 inches to about 0.008 inches but not limited to any particular diameter or shaped factor may result in correction of asymmetry.

In another embodiment, asymmetry is overcome through the use of a staggered wave parting line as discussed earlier. For example, at least a portion or all of the dimples adjacent the parting line are aligned with and positioned to overlap corresponding dimples across the parting line.

While it is apparent that the illustrative embodiments of the invention herein disclosed fulfill the objectives stated above, it will be appreciated that numerous modifications and other embodiments may be devised by those skilled in the art.

For example, as used herein, the term “dimple”, may include any texturizing on the surface of a golf ball, e.g., depressions and extrusions. Some non-limiting examples of depressions and extrusions include, but are not limited to, spherical depressions, meshes, raised ridges, and brambles. The depressions and extrusions may take a variety of plan-form shapes, such as circular, polygonal, oval, or irregular. Dimples that have multi-level configurations, i.e., dimple within a dimple, are also contemplated by the invention to obtain desirable aerodynamic characteristics. As such, while the majority of the discussion relating to dimples herein relates to those dimples having profiles based on a catenary curve, other types of dimples fitting the definition in this paragraph are contemplated for use in any portions of the golf ball surface not covered by dimples with catenary curve profiles.

Therefore, it will be understood that the appended claims are intended to cover all such modifications and embodiments which come within the spirit and scope of the present invention.

What is claimed is:

1. A golf ball having a plurality of recessed dimples on the surface thereof, wherein at least a portion of the plurality of recessed dimples have a profile defined by the revolution of a catenary curve according to the following function:

$$y = \frac{d_c(\cosh(sf * x) - 1)}{\cosh\left(sf * \frac{D}{2}\right) - 1}$$

wherein y is the vertical direction coordinate away from the center of the ball with 0 at the center of the dimple;

x is the horizontal (radial) direction coordinate from the dimple apex to the dimple surface with 0 at the center of the dimple;

sf is a shape factor;

d_c is the chordal depth of the dimple; and

D is the diameter of the dimple.

2. The golf ball of claim 1, wherein at least a portion comprises about 50 percent or more of the dimples on the golf ball.

3. The golf ball of claim 1, wherein at least a portion comprises about 80 percent or more of the dimples on the golf ball.

4. The golf ball of claim 1, wherein sf is from about 5 to about 200.

5. The golf ball of claim 4, wherein sf is from about 10 to about 100.

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6. The golf ball of claim 4, wherein sf is from about 10 to about 75.

7. The golf ball of claim 1, wherein D is between about 0.115 inches and about 0.185 inches.

8. The golf ball of claim 1, wherein D is between about 0.125 inches and about 0.185 inches.

9. The golf ball of claim 1, wherein d_c is from about 0.002 inches to about 0.008 inches.

10. The golf ball of claim 9, wherein d_c is from about 0.004 inches to about 0.006 inches.

11. The golf ball of claim 1, wherein D is between about 0.115 inches and about 0.185 inches, sf is from about 10 to 100, and d_c is from about 0.004 inches to about 0.006 inches.

12. A golf ball having a plurality of recessed dimples on the surface thereof, wherein at least a portion of the plurality of recessed dimples have a profile defined by the revolution of a catenary curve according to the following function:

$$y = \frac{d_c sf^2}{2 \left(\cosh \left(sf \frac{D}{2} \right) - 1 \right)} * x^2 + \frac{d_c sf^4}{24 \left(\cosh \left(sf \frac{D}{2} \right) - 1 \right)} * x^4 \quad 20$$

wherein y is the vertical direction coordinate away from the center of the ball with 0 at the center of the dimple;

x is the horizontal (radial) direction coordinate from the dimple apex to the dimple surface with 0 at the center of the dimple;

sf is a shape factor and less than or equal to about 50;

d_c is the chordal depth of the dimple; and

D is the diameter of the dimple.

13. The golf ball of claim 12, wherein d_c is from about 0.002 inches to about 0.010 inches.

14. The golf ball of claim 13, wherein d_c is from about 0.003 inches to about 0.009 inches.

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15. The golf ball of claim 12, wherein the at least a portion comprises about 50 percent or more of the dimples on the golf ball.

16. The golf ball of claim 15, wherein the at least a portion comprises about 80 percent or more of the dimples on the golf ball.

17. A golf ball having a plurality of recessed dimples on the surface thereof, wherein at least a portion of the plurality of recessed dimples have a profile defined by the revolution of a catenary curve according to the following function:

$$y = \frac{d_c \left(\sqrt{1 + \sinh^2 (sf * x)} - 1 \right)}{\sqrt{1 + \sinh^2 \left(sf * \frac{D}{2} \right)} - 1} \quad 15$$

wherein y is the vertical direction coordinate away from the center of the ball with 0 at the center of the dimple;

x is the horizontal (radial) direction coordinate from the dimple apex to the dimple surface with 0 at the center of the dimple;

sf is a shape factor;

d_c is the chordal depth of the dimple; and

D is the diameter of the dimple.

18. The golf ball of claim 17, wherein the at least a portion comprises about 50 percent or more of the dimples on the golf ball.

19. The golf ball of claim 17, wherein d_c is from about 0.003 inches to about 0.009 inches.

20. The golf ball of claim 17, wherein sf ranges from about 10 to about 100.

* * * * *

Exhibit J

(12) **United States Patent**
Aoyama et al.

(10) **Patent No.:** **US 7,641,572 B2**
(45) **Date of Patent:** **Jan. 5, 2010**

(54) **GOLF BALL DIMPLES WITH A CATENARY CURVE PROFILE**

(75) Inventors: **Steven Aoyama**, Fairhaven, MA (US);
Nicholas M. Nardacci, Fairhaven, MA (US)

(73) Assignee: **Acushnet Company**, Fairhaven, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **12/071,087**

(22) Filed: **Feb. 15, 2008**

(65) **Prior Publication Data**

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Related U.S. Application Data

(60) Continuation-in-part of application No. 11/907,195, filed on Oct. 10, 2007, now Pat. No. 7,491,137, which is a continuation of application No. 11/607,916, filed on Dec. 4, 2006, now abandoned, which is a continuation of application No. 11/108,812, filed on Apr. 19, 2005, now Pat. No. 7,156,757, which is a continuation of application No. 10/784,744, filed on Feb. 24, 2004, now Pat. No. 6,913,550, which is a continuation of application No. 10/096,852, filed on Mar. 14, 2002, now Pat. No. 6,729,976, which is a continuation-in-part of application No. 09/989,191, filed on Nov. 21, 2001, now Pat. No. 6,796,912, and a continuation-in-part of application No. 09/404,164, filed on Sep. 27, 1999, now Pat. No. 6,358,161, which is a division of application No. 08/922,633, filed on Sep. 3, 1997, now Pat. No. 5,957,786.

(51) **Int. Cl.**
A63B 37/12 (2006.01)

(52) **U.S. Cl.** **473/383**

(58) **Field of Classification Search** 473/383–385
See application file for complete search history.

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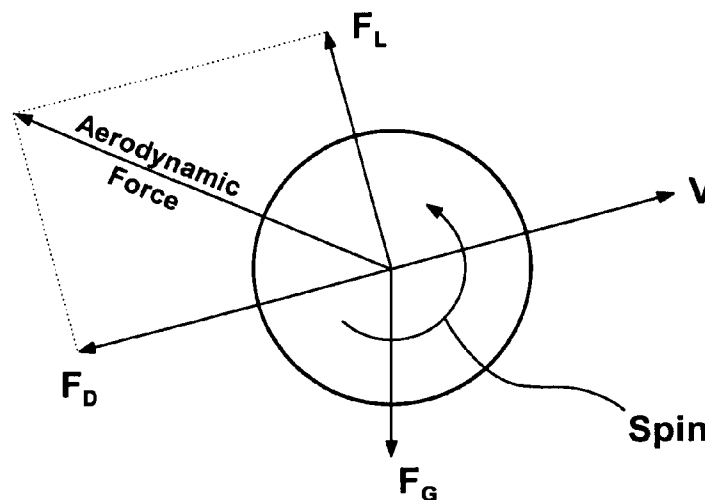
Primary Examiner—Raeann Trimiew

(74) *Attorney, Agent, or Firm*—Hanify & King, P.C.

(57) **ABSTRACT**

A golf ball having an outside surface with a plurality of dimples formed thereon. The dimples on the ball have a cross-sectional profiles formed by a catenary curve. Combinations of varying dimple diameters, shape factors, and chordal depths in the catenary curve are used to vary the ball flight performance according to ball spin characteristics, player swing speed, as well as satisfy specific aerodynamic magnitude and direction criteria.

19 Claims, 22 Drawing Sheets



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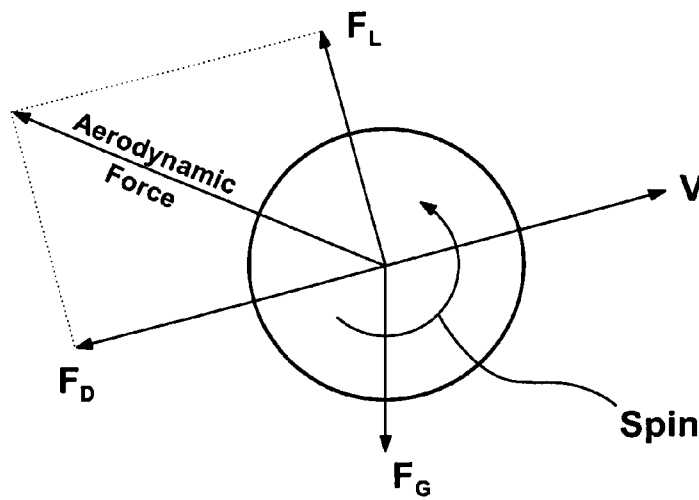


FIG. 1

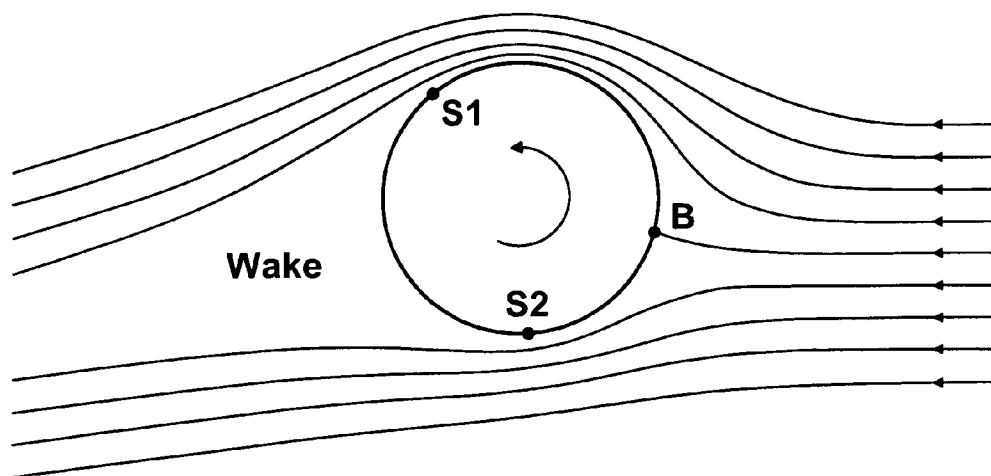


FIG. 2

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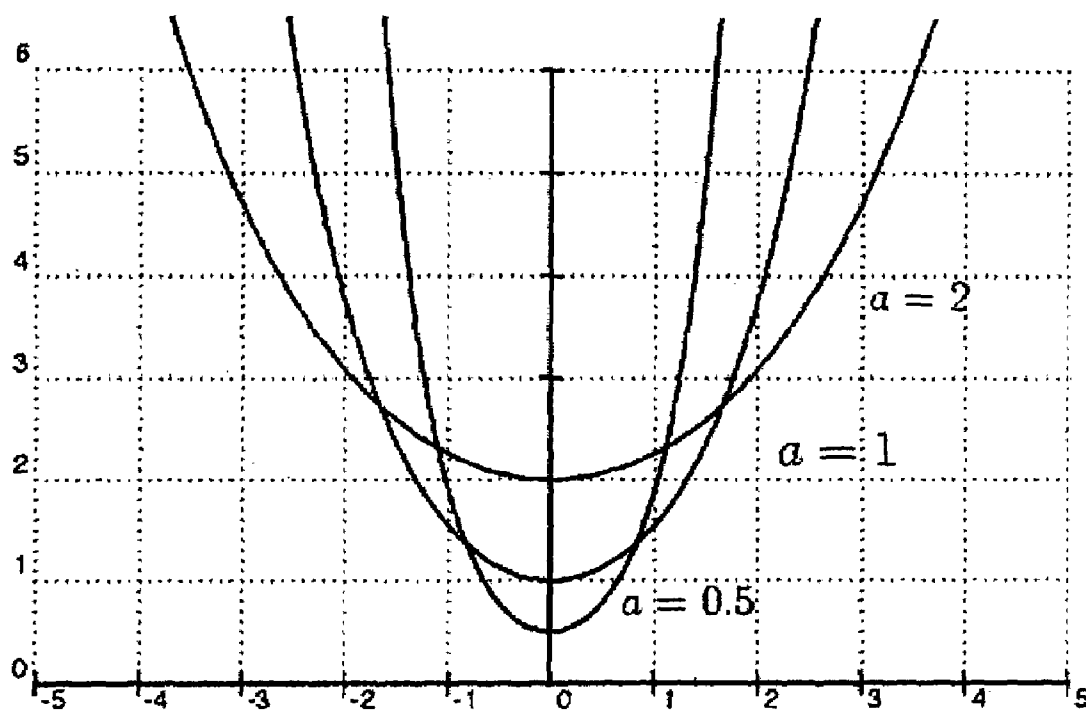


FIG. 3

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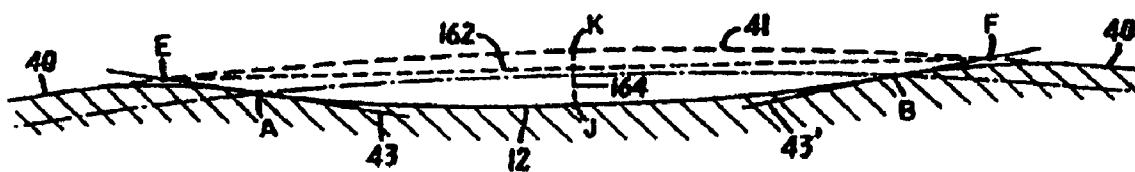


FIG. 4

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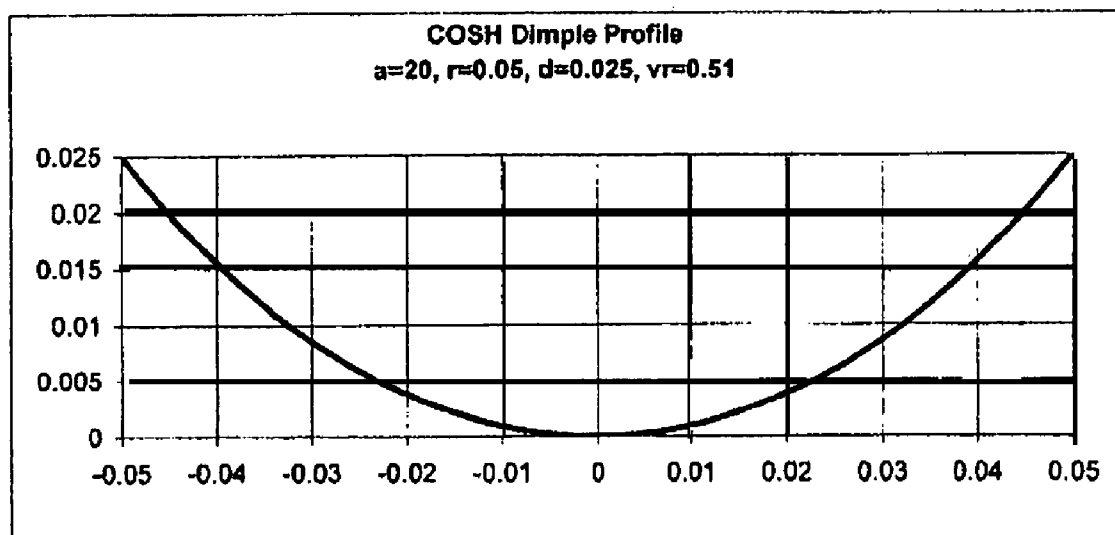


FIG. 5

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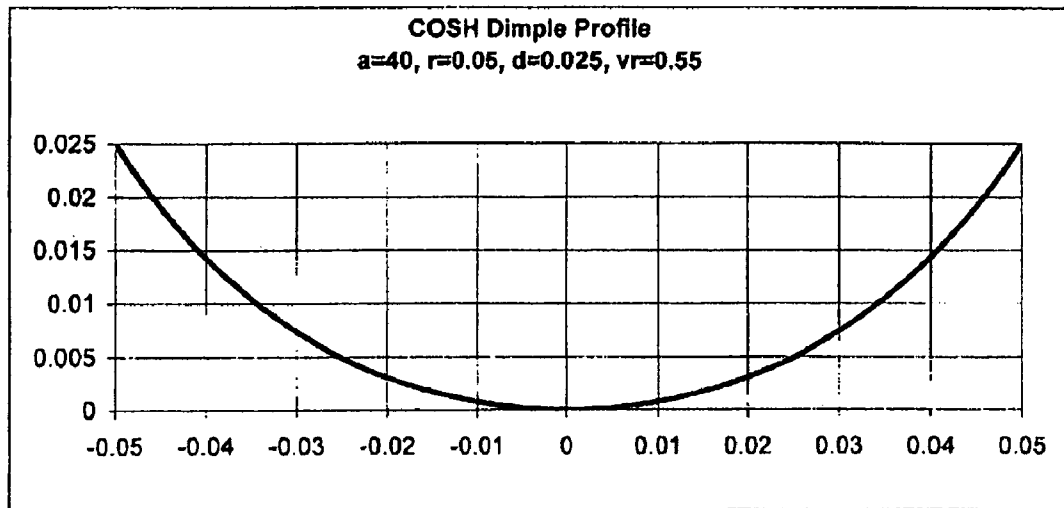


FIG. 6

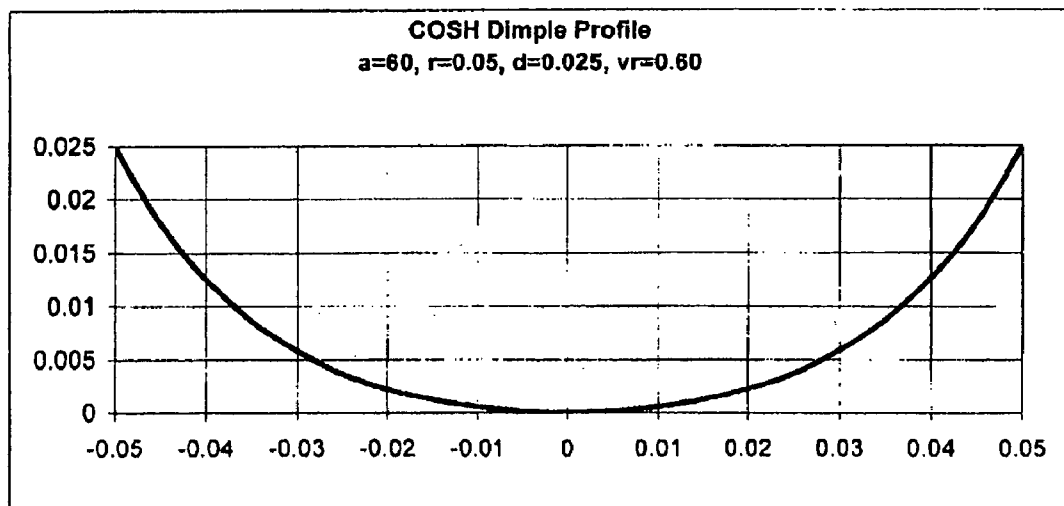


FIG. 7

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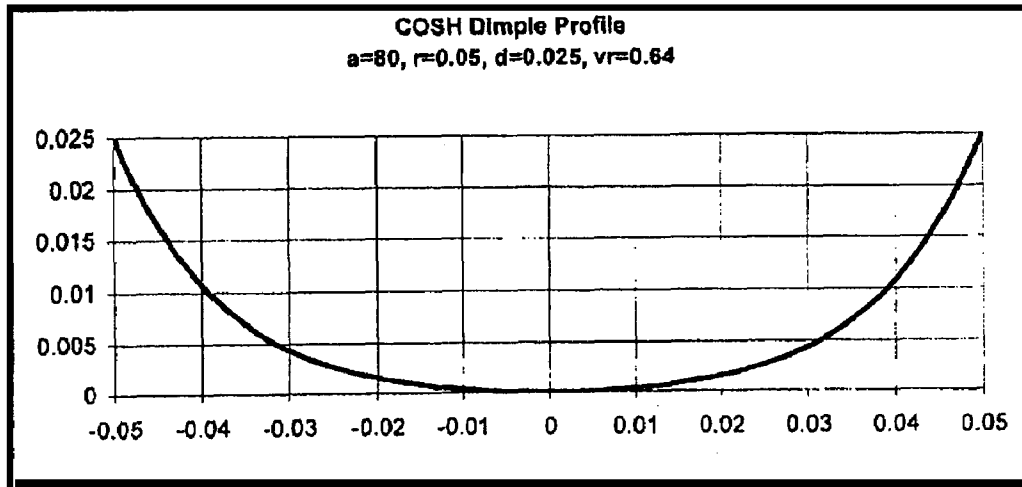


FIG. 8

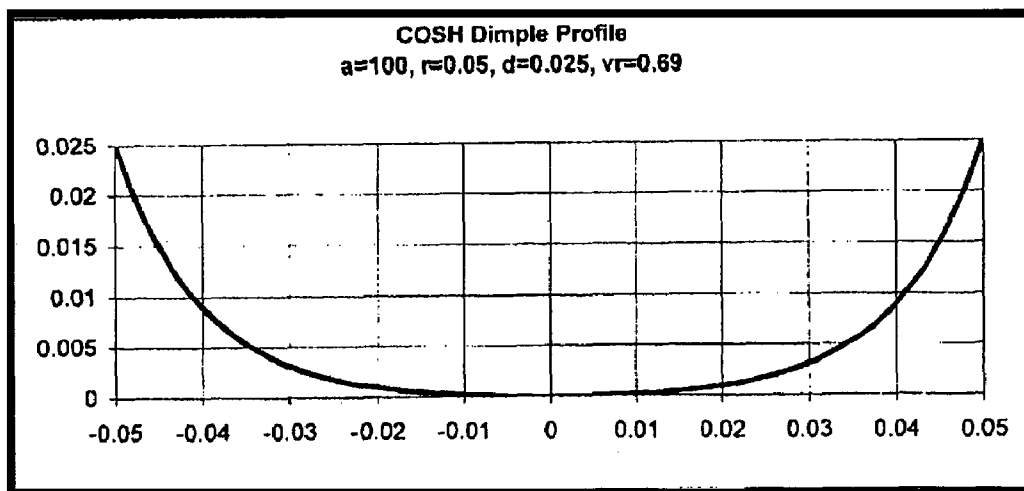


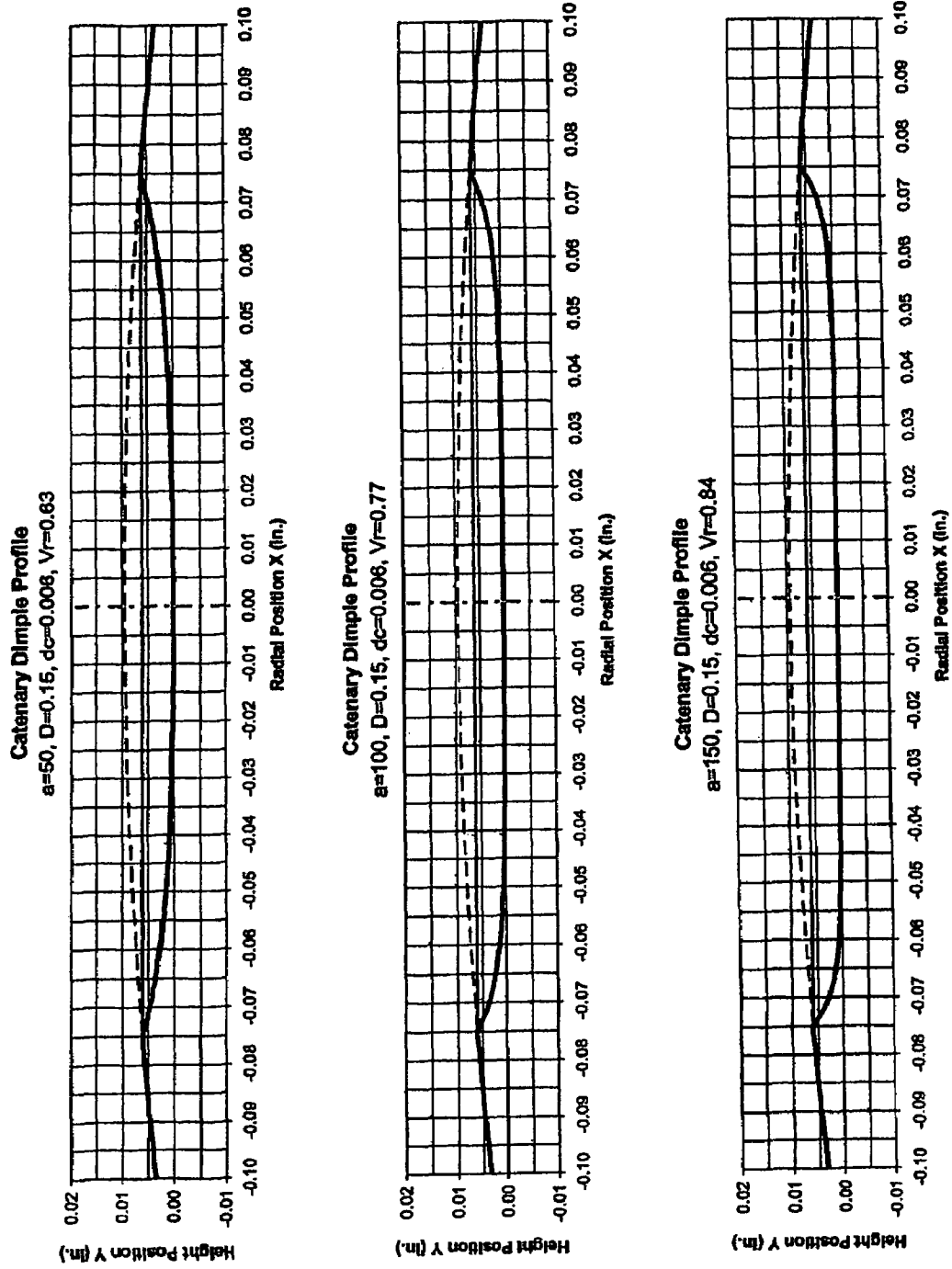
FIG. 9

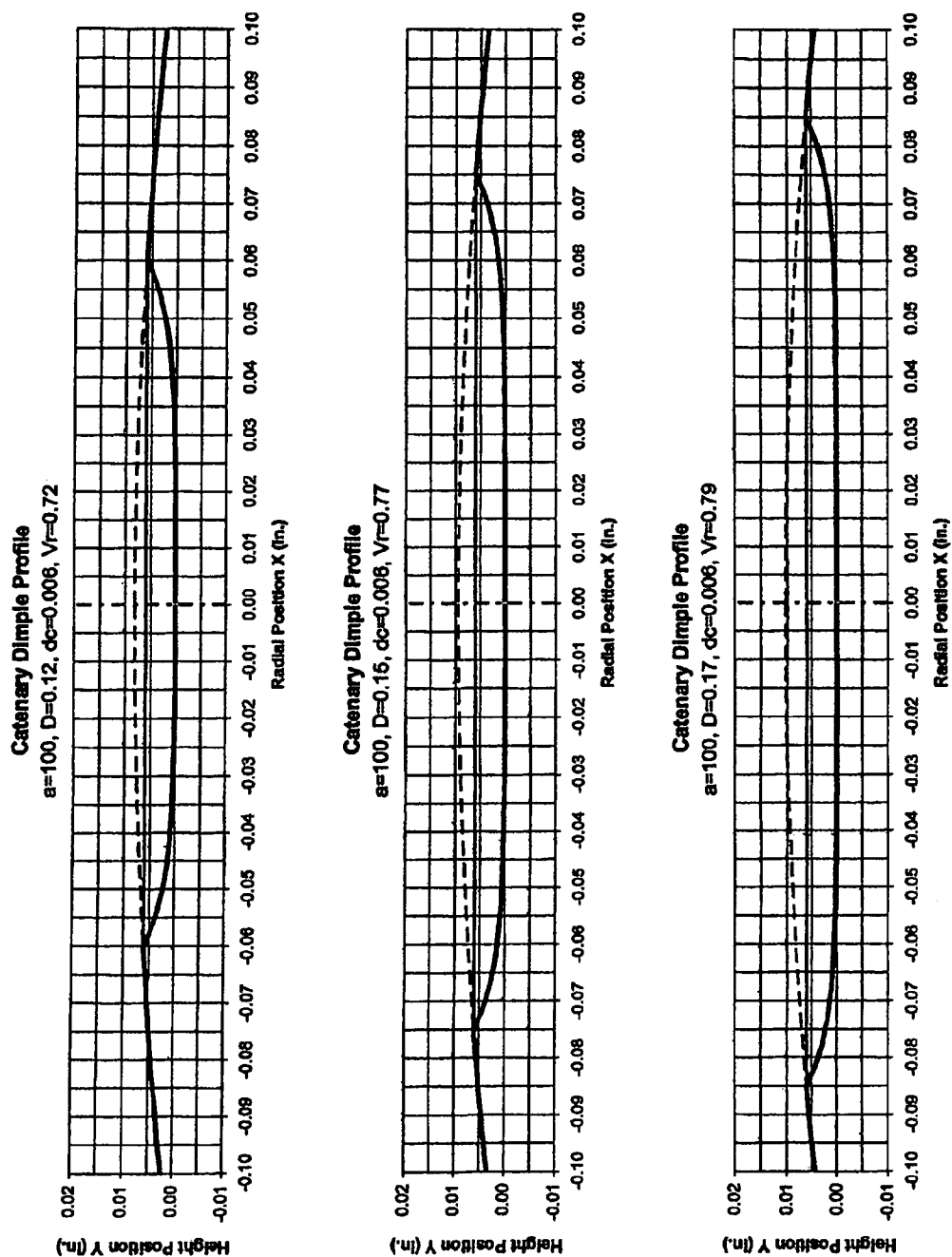
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**FIG. 10**

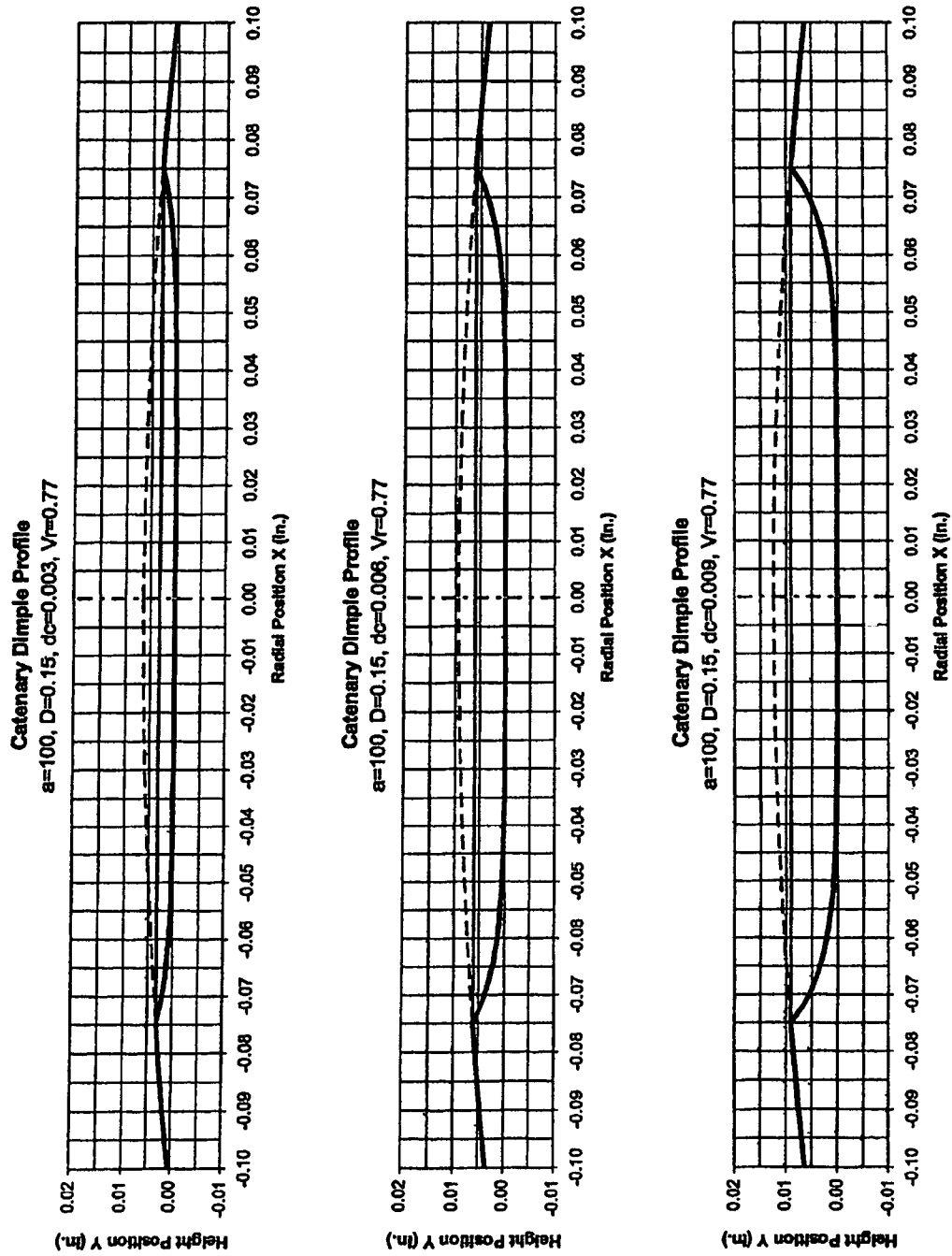
**FIG. 11**

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**FIG. 12**

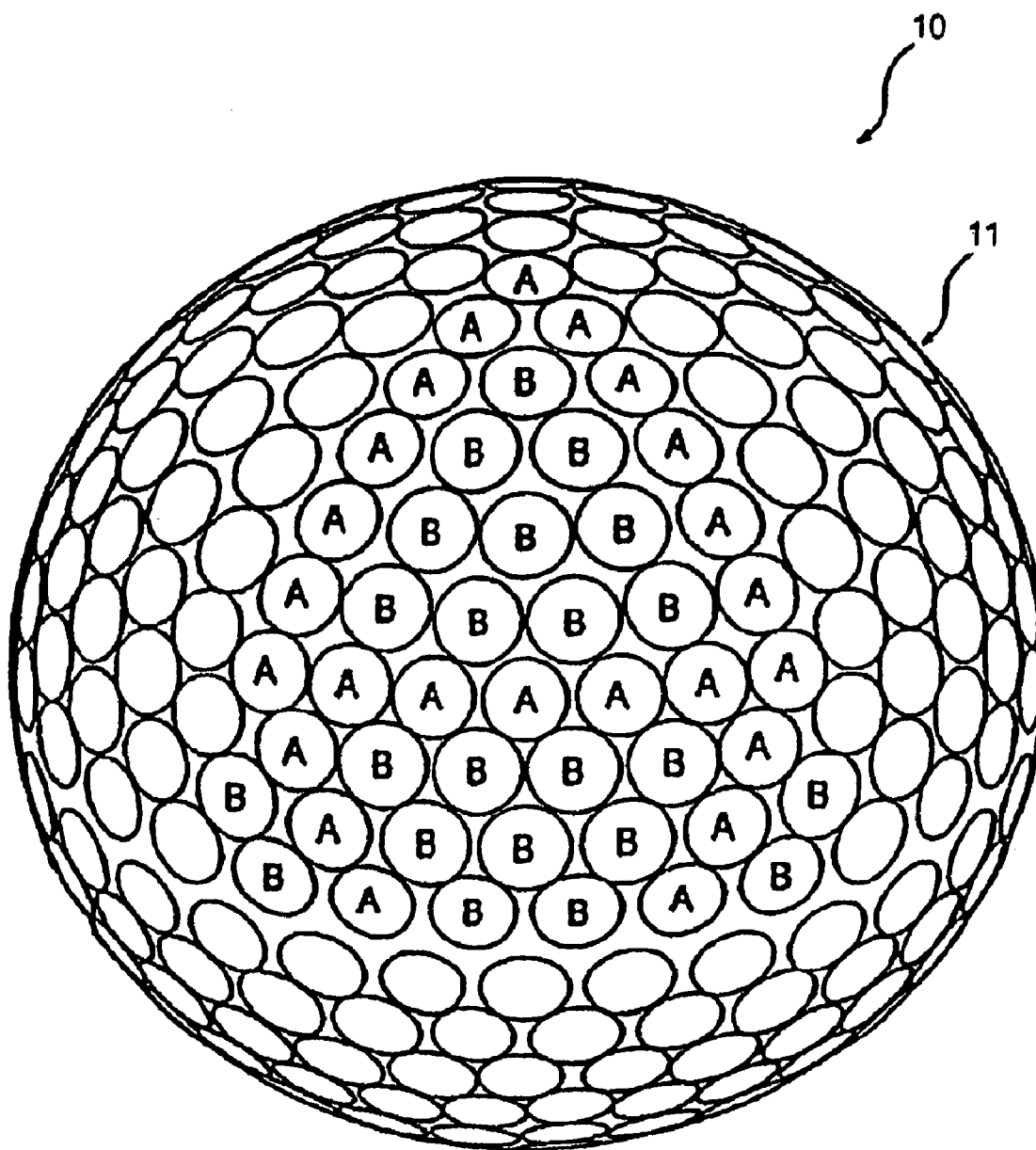


FIG. 13

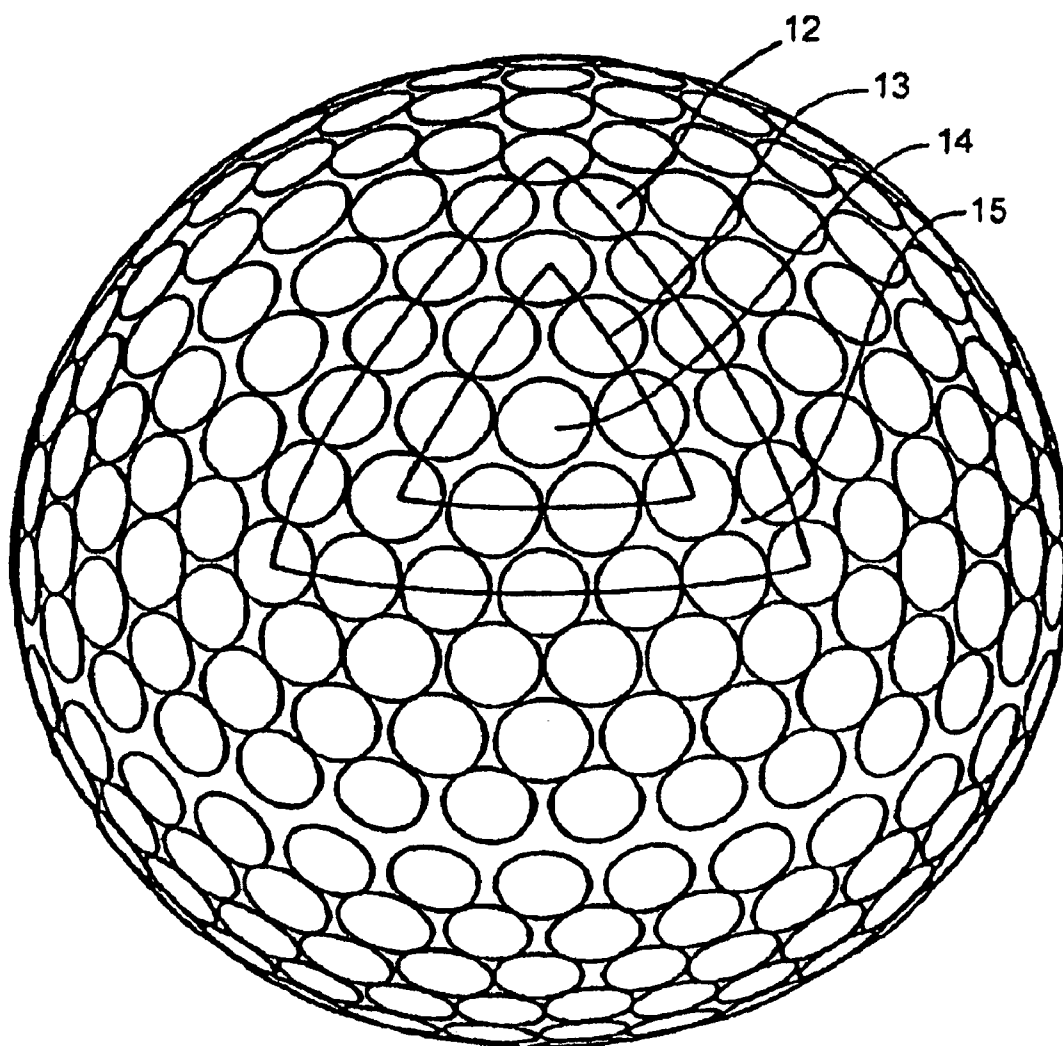


FIG. 14

$D_A < D_B \leq D_C \leq D_D \leq D_E$
 $80\% D_A, D_B, D_C, D_D, D_E > 0.11"$
 DIMP. AREA > 80%

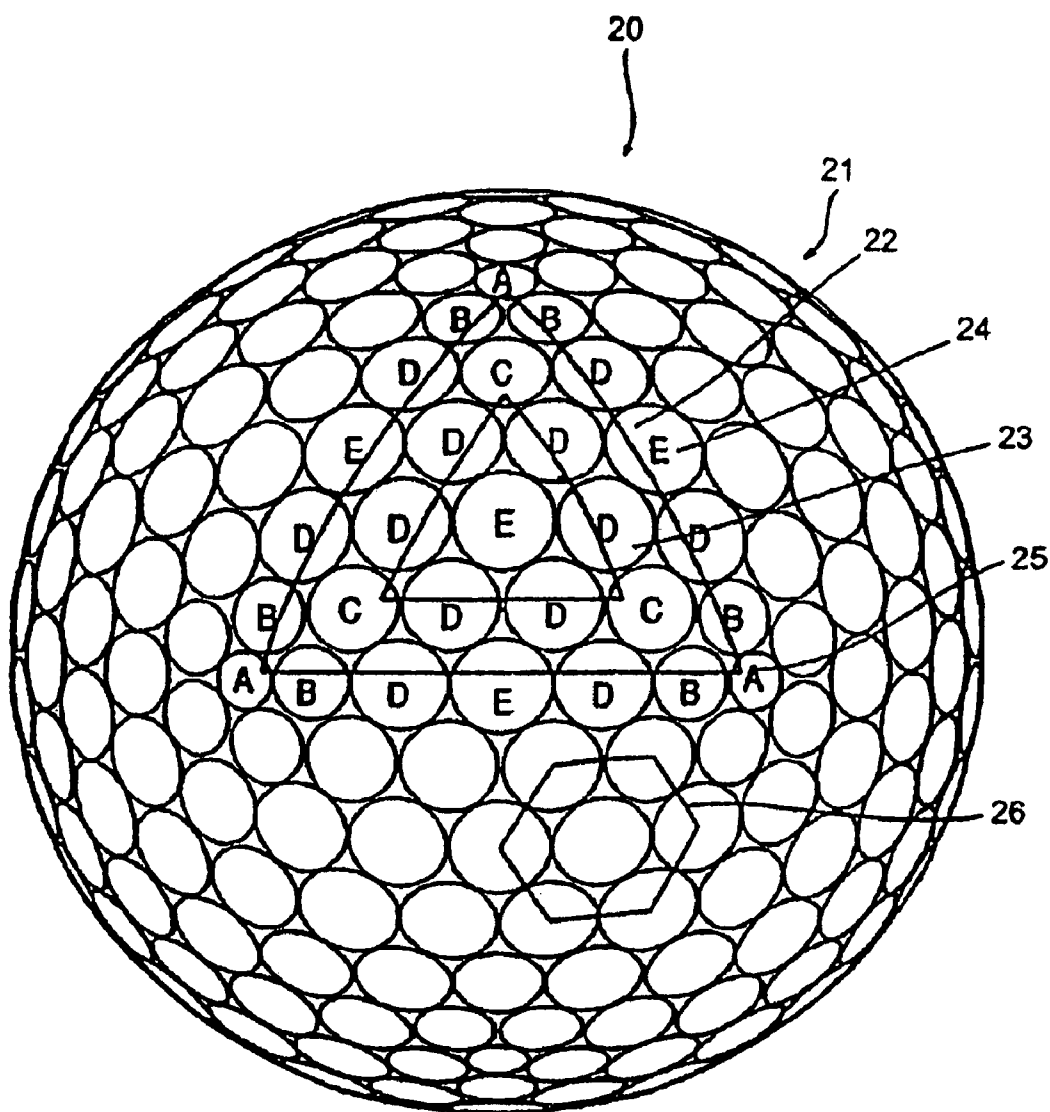


FIG. 15

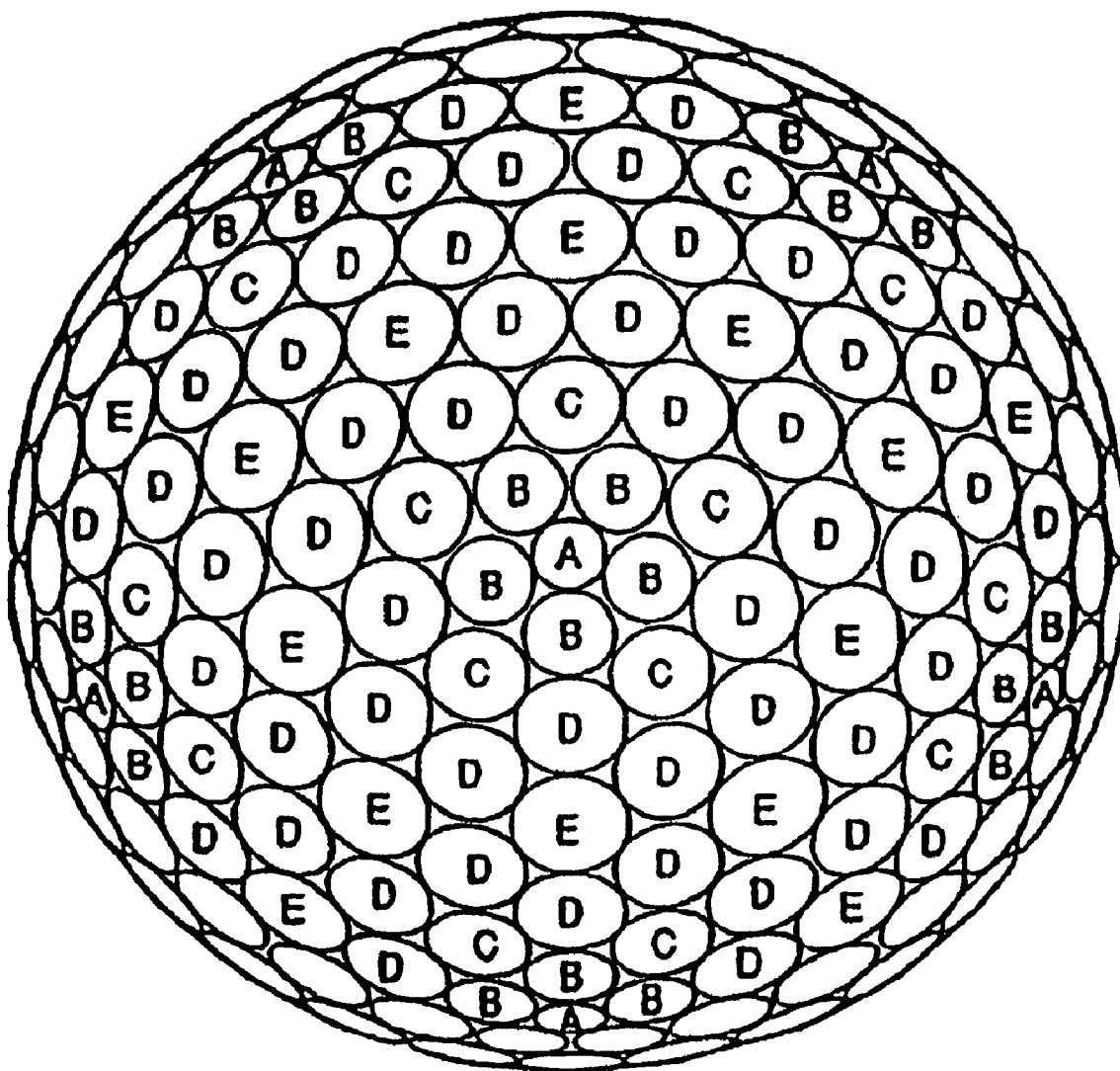


FIG. 16

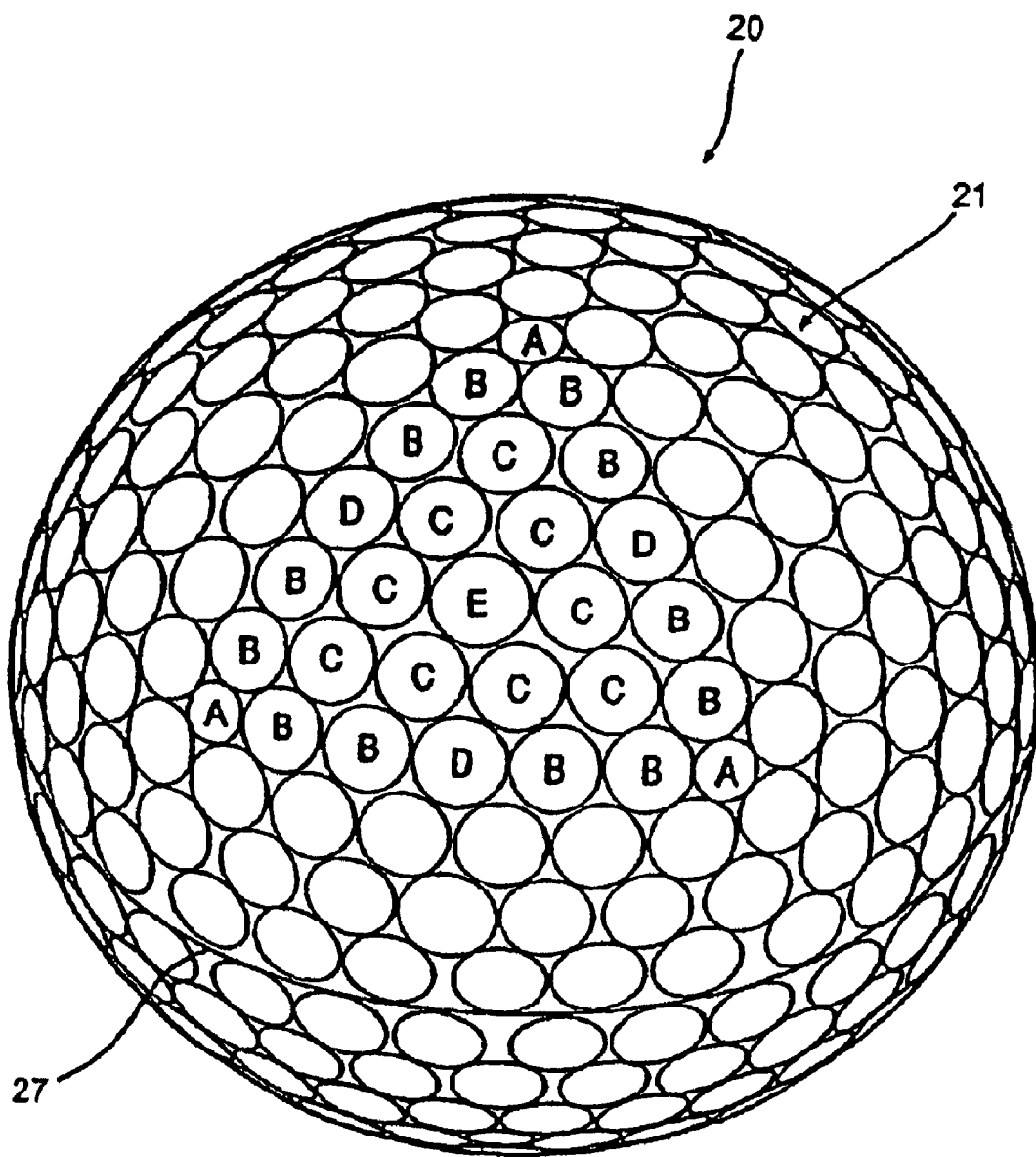


FIG. 17

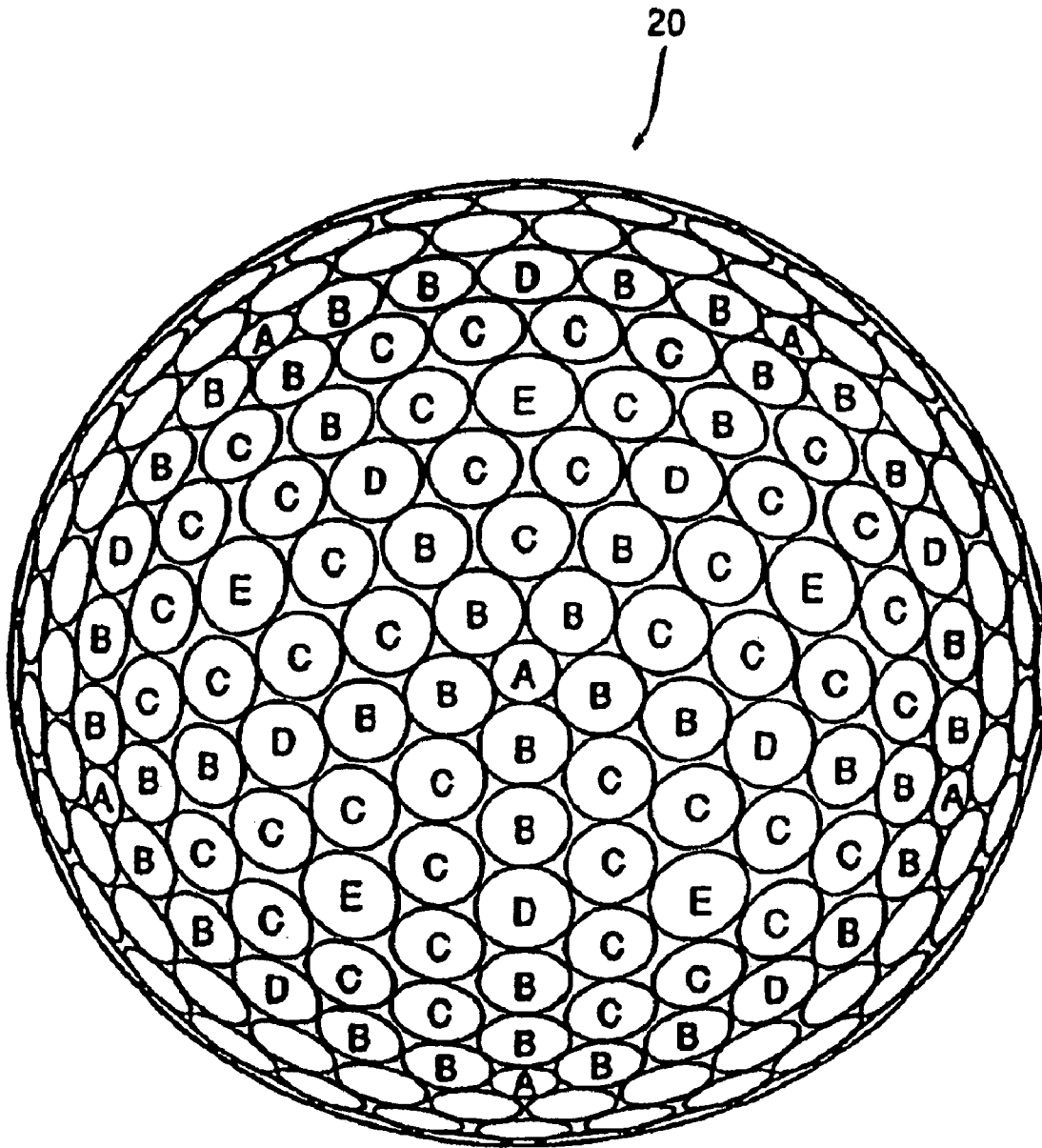


FIG. 18

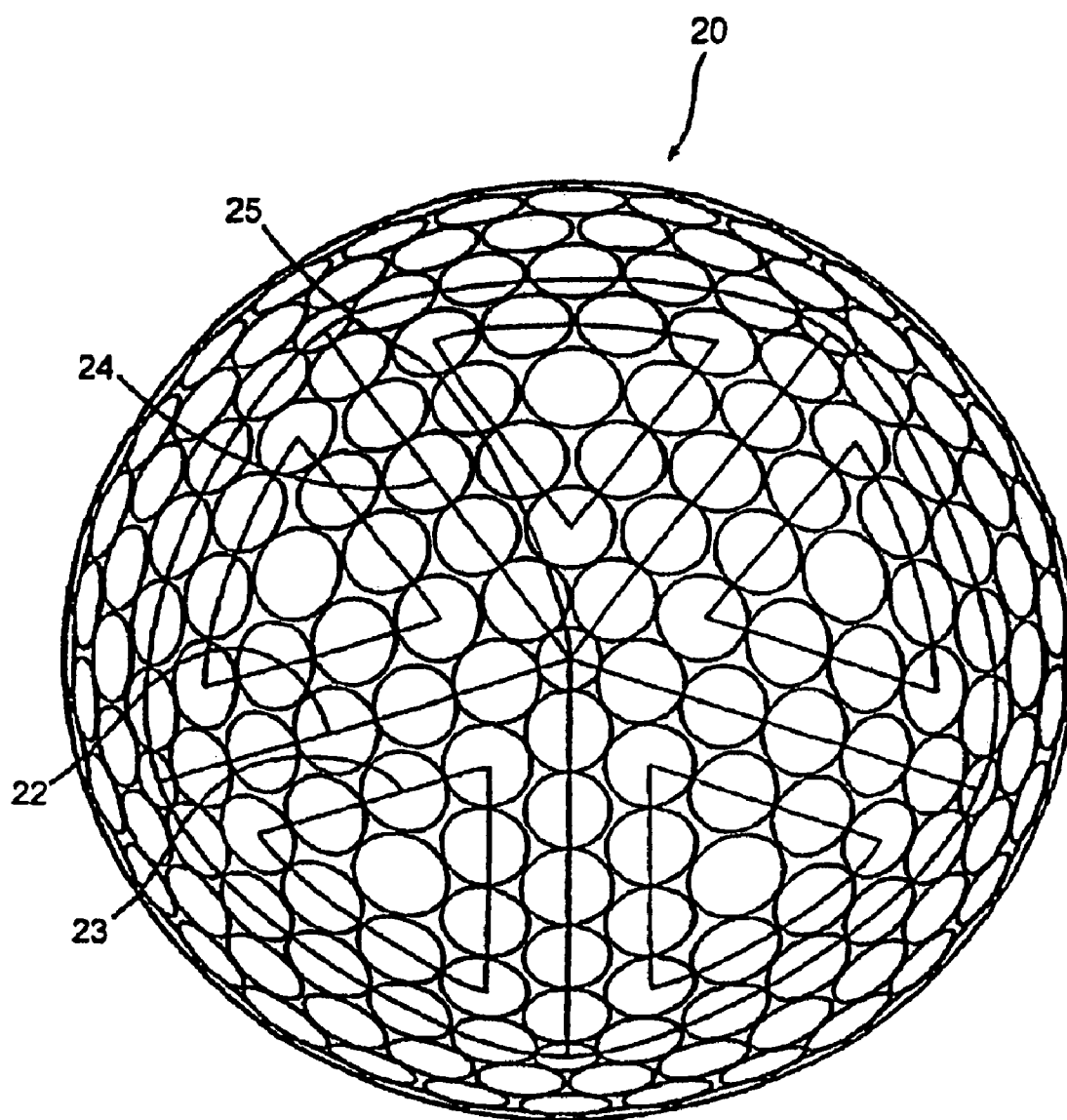


FIG. 19

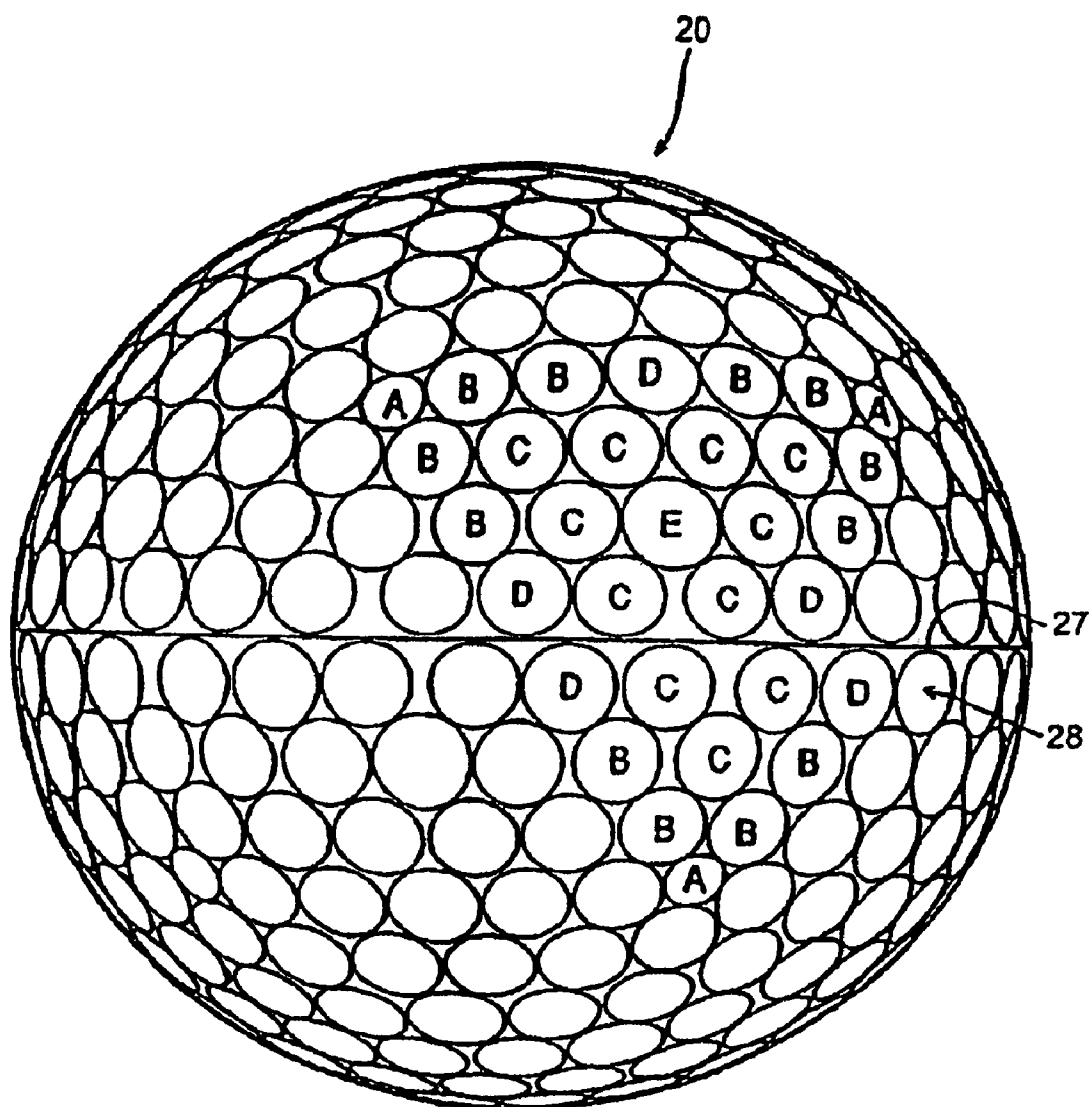


FIG. 20



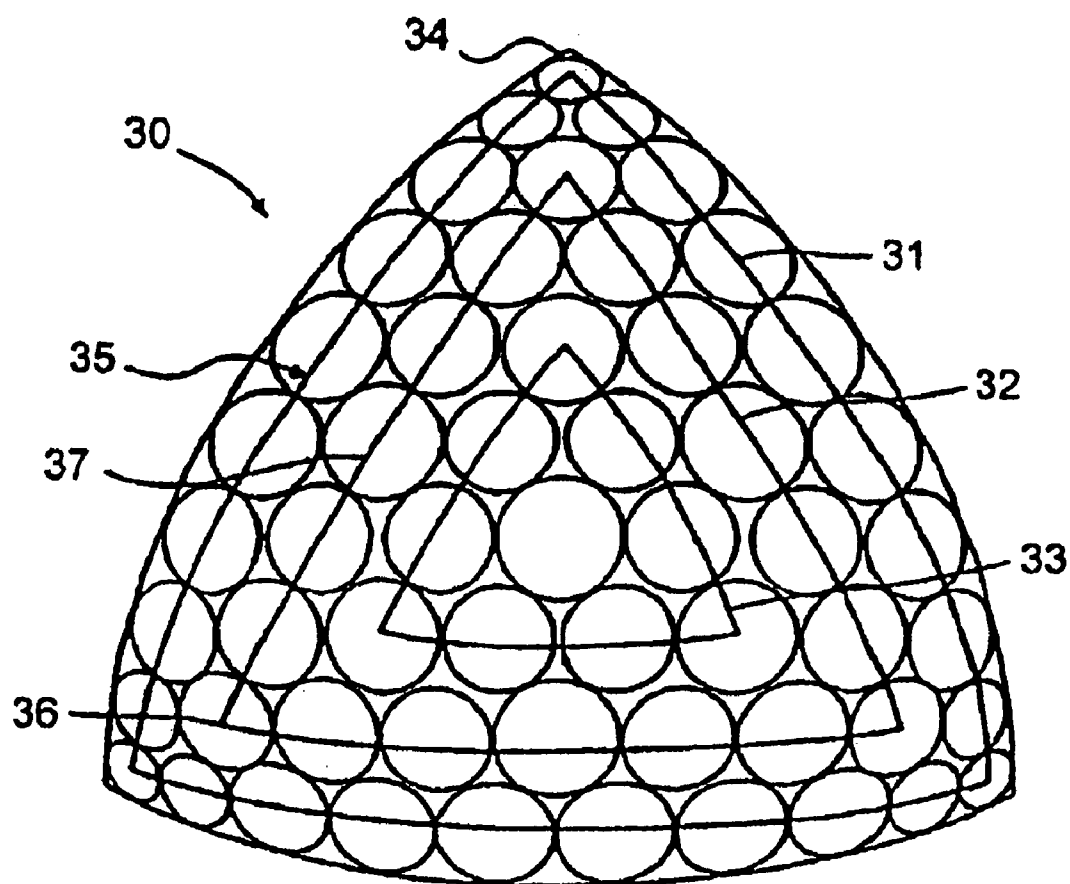
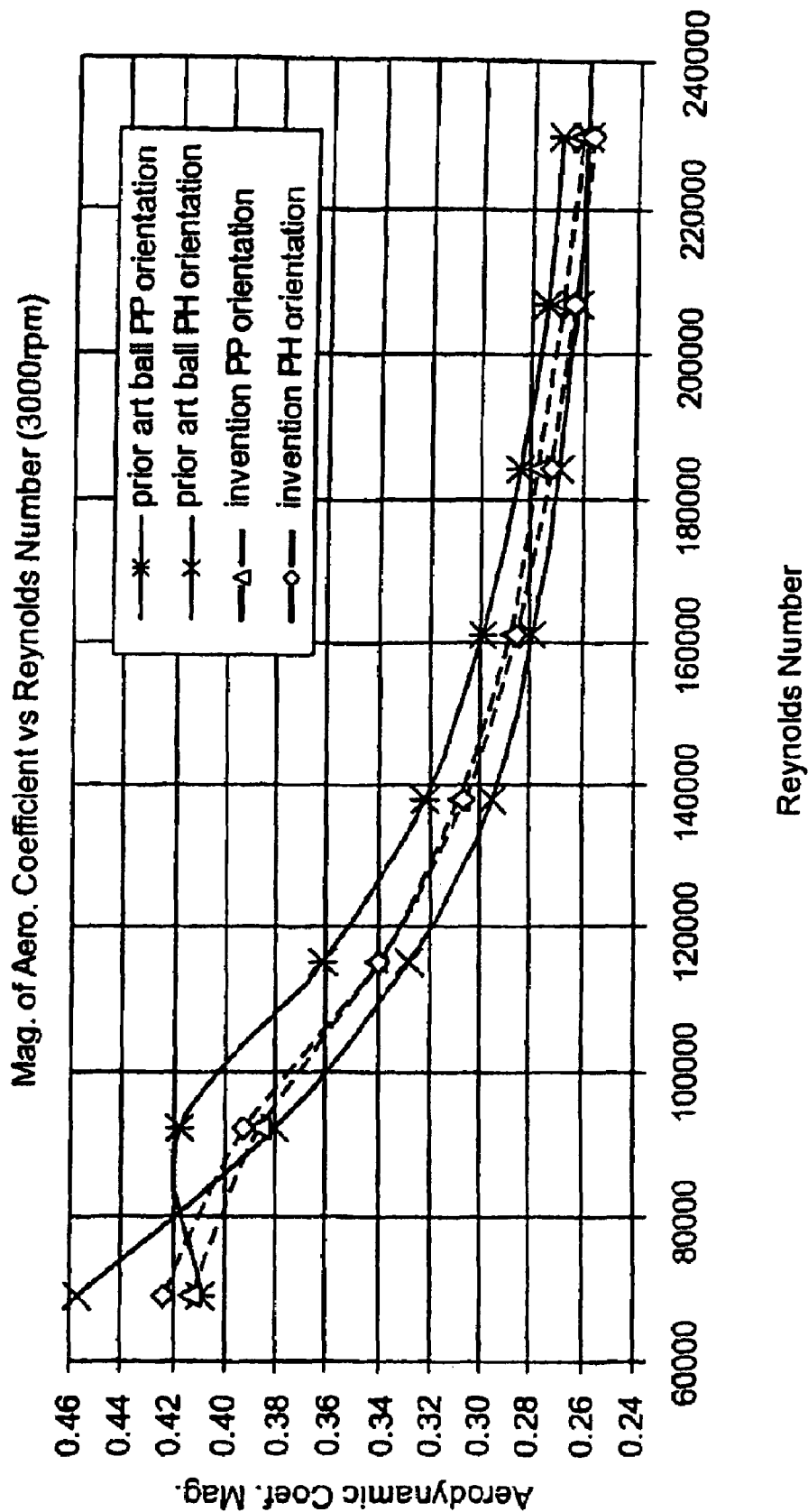
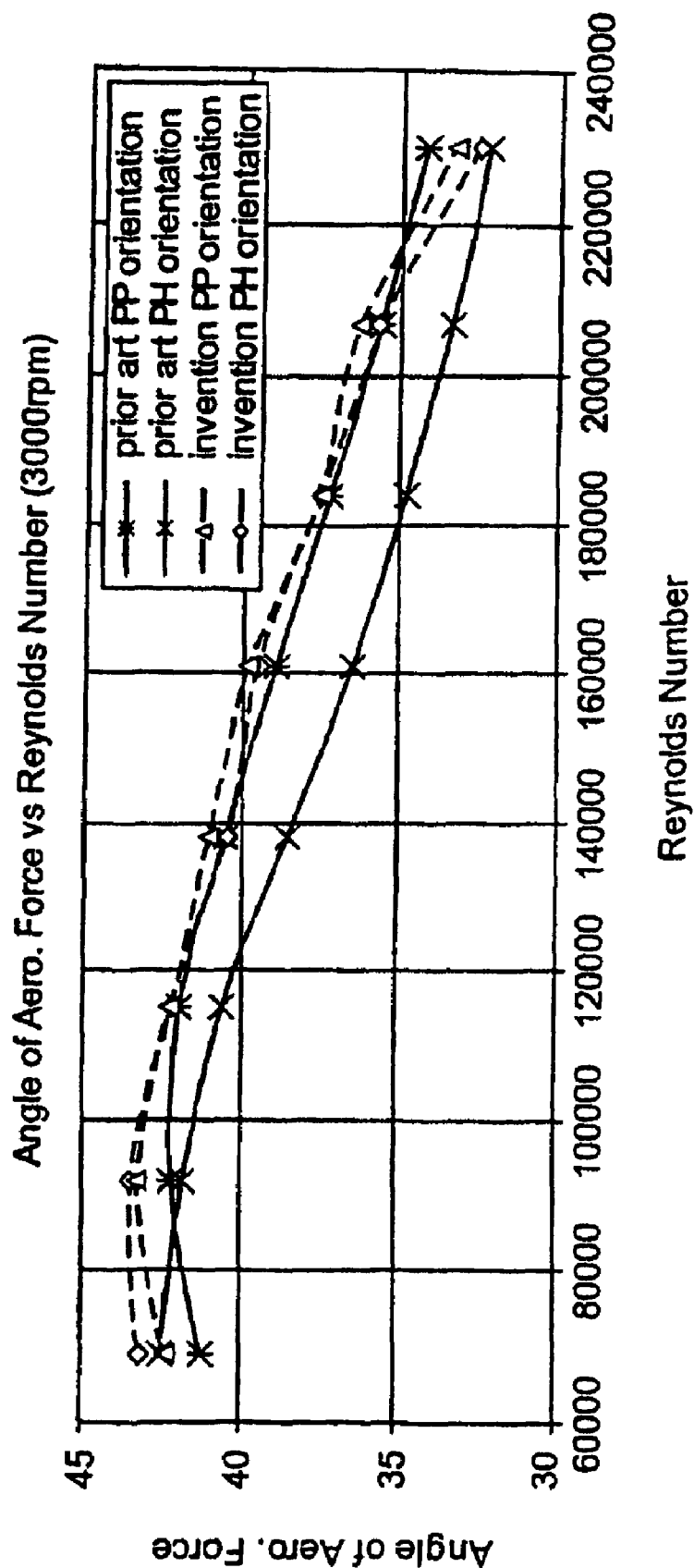


FIG. 22

**FIG. 23**

**FIG. 24**

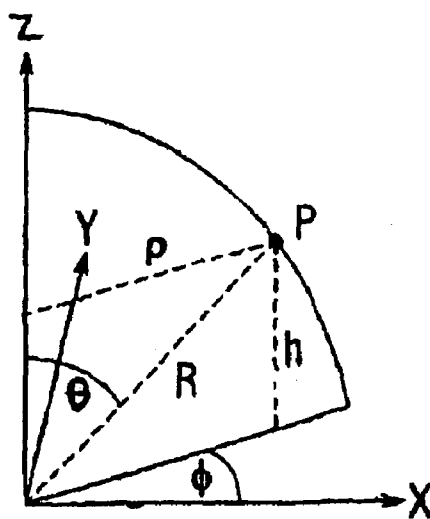


FIG. 25

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GOLF BALL DIMPLES WITH A CATENARY CURVE PROFILE**CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is a continuation-in-part of U.S. application Ser. No. 11/907,195, filed Oct. 10, 2007 now U.S. Pat. No. 7,491,137, which is a continuation of U.S. patent application Ser. No. 11/607,916, filed Dec. 04, 2006 now abandoned, which is a continuation of U.S. patent application Ser. No. 11/108,812, filed Apr. 19, 2005 now U.S. Pat. No. 7,156,757, which is a continuation of U.S. patent application Ser. No. 10/784,744, filed Feb. 24, 2004, now U.S. Pat. No. 6,913,550, which is a continuation of U.S. patent application Ser. No. 10/096,852, filed Mar. 14, 2002, now U.S. Pat. No. 6,729,976, which is a continuation-in-part of U.S. patent application Ser. No. 09/989,191, filed Nov. 21, 2001, now U.S. Pat. No. 6,796,912, and also a continuation-in-part of U.S. patent application Ser. No. 09/404,164, filed Sep. 27, 1999, now U.S. Pat. No. 6,358,161, which is a divisional of U.S. patent application Ser. No. 08/922,633, filed Sep. 3, 1997, now U.S. Pat. No. 5,957,786. The entire disclosures of the related applications are incorporated by reference herein.

FIELD OF INVENTION

The present invention relates to golf balls having improved aerodynamic characteristics that yield improved flight performance and longer ball flight. The improved aerodynamic characteristics are obtained through the use of specific dimple arrangements and dimple profiles. In particular, the invention relates to a dimple pattern including dimples having a cross-sectional profile defined by a mathematical function based on a catenary curve. The use of such a cross-sectional profile provides improved means to control dimple shape, volume, and transition to a spherical golf ball surface. The aerodynamic improvements are applicable to golf balls of any size and weight.

BACKGROUND OF THE INVENTION

The flight of a golf ball is determined by many factors. The majority of the properties that determine flight are outside of the control of the golfer. While a golfer can control the speed, the launch angle, and the spin rate of a golf ball by hitting the ball with a particular club, the final resting point of the ball depends upon golf ball construction and materials, as well as environmental conditions, e.g., terrain and weather. Since flight distance and consistency are critical factor in reducing golf scores, manufacturers continually strive to make even the slightest incremental improvements in golf ball flight consistency and flight distance, e.g., one or more yards, through various aerodynamic properties and golf ball constructions. For example, golf balls were originally made with smooth outer surfaces. However, in the late nineteenth century, players observed that, as golf balls became scuffed or marred from play, the balls achieved more distance. As such, players then began to roughen the surface of new golf balls with a hammer to increase flight distance.

Manufacturers soon caught on and began molding non-smooth outer surfaces on golf balls. By the mid 1900's, almost every golf ball being made had 336 dimples arranged in an octahedral pattern. Generally, these balls had about 60 percent of their outer surface covered by dimples. Over time, improvements in ball performance were developed by utilizing different dimple patterns. In 1983, for instance, Titleist

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introduced the TITLEIST 384, which had 384 dimples that were arranged in an icosahedral pattern resulting in about 76 percent coverage of the ball surface. The dimpled golf balls used today travel nearly two times farther than a similar ball without dimples.

These improvements have come at great cost to manufacturers. In fact, historically manufacturers improved flight performance via iterative testing, where golf balls with numerous dimple patterns and dimple profiles are produced and tested using mechanical golfers. Flight performance is characterized in these tests by measuring the landing position of the various ball designs. For example, to determine if a particular ball design has desirable flight characteristics for a broad range of players, i.e., high and low swing speed players, manufacturers perform the mechanical golfer test with different ball launch conditions, which involves immense time and financial commitments. Furthermore, it is difficult to identify incremental performance improvements using these methods due to the statistical noise generated by environmental conditions, which necessitates large sample sizes for sufficient confidence intervals.

Another more precise method of determining specific dimple arrangements and dimple shapes, that result in an aerodynamic advantage, involves the direct measurement of aerodynamic characteristics as opposed to ball landing positions. These aerodynamic characteristics define the forces acting upon the golf ball throughout flight.

Aerodynamic forces acting on a golf ball are typically resolved into orthogonal components of lift (F_L) and drag (F_D). FIG. 1 shows the various forces acting on a golf ball in flight. Lift is defined as the aerodynamic force component acting perpendicular to the flight path. It results from a difference in pressure that is created by a distortion in the air flow that results from the back spin of the ball. A boundary layer forms at the stagnation point of the ball, B, then grows and separates at points S1 and S2, as shown in FIG. 2. Due to the ball backspin, the top of the ball moves in the direction of the airflow, which retards the separation of the boundary layer. In contrast, the bottom of the ball moves against the direction of airflow, thus advancing the separation of the boundary layer at the bottom of the ball. Therefore, the position of separation of the boundary layer at the top of the ball, S1, is further back than the position of separation of the boundary layer at the bottom of the ball, S2. This asymmetrical separation creates an arch in the flow pattern, requiring the air over the top of the ball to move faster and, thus, have lower pressure than the air underneath the ball.

Drag is defined as the aerodynamic force component acting parallel to the ball flight direction. As the ball travels through the air, the air surrounding the ball has different velocities and, accordingly, different pressures. The air exerts maximum pressure at the stagnation point, B, on the front of the ball, as shown in FIG. 2. The air then flows over the sides of the ball and has increased velocity and reduced pressure. The air separates from the surface of the ball at points S1 and S2, leaving a large turbulent flow area with low pressure, i.e., the wake. The difference between the high pressure in front of the ball and the low pressure behind the ball reduces the ball speed and acts as the primary source of drag for a golf ball.

The dimples on a golf ball are important in reducing drag and increasing lift. For example, the dimples on a golf ball create a turbulent boundary layer around the ball, i.e., the air in a thin layer adjacent to the ball flows in a turbulent manner. The turbulence energizes the boundary layer and helps it stay attached further around the ball to reduce the area of the wake. This greatly increases the pressure behind the ball and substantially reduces the drag.

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Based on the role that dimples play in reducing drag on a golf ball, golf ball manufacturers continually seek dimple patterns that increase the distance traveled by a golf ball. A high degree of dimple coverage is beneficial to flight distance, but only if the dimples are of a reasonable size. Dimple coverage gained by filling spaces with tiny dimples is not very effective, since tiny dimples are not good turbulence generators.

In addition to researching dimple pattern and size, golf ball manufacturers also study the effect of dimple shape, volume, and cross-section on overall flight performance of the ball. One example is U.S. Pat. No. 5,735,757, which discusses making dimples using two different spherical radii with an "inflection point" where the two curves meet. In most cases, however, the cross-sectional profiles of dimples in prior art golf balls are spherical, parabolic, elliptical, semi-spherical curves, saucer-shaped, a sine curve, a truncated cone, or a flattened trapezoid. One disadvantage of these shapes is that they can sharply intrude into the surface of the ball, which may cause the drag to become excessive. As a result, the ball may not make best use of momentum initially imparted thereto, resulting in an insufficient carry of the ball.

Further, the most commonly used spherical profile is essentially a function of two parameters: diameter and depth (chordal or surface). While edge angle, which is a measure of the steepness of the dimple wall where it abuts the ball surface, is often discussed when describing these types of profiles, edge angle generally cannot be varied independently of depth unless dual radius profiles are employed. The cross sections of dual radius dimple profiles are generally defined by two circular arcs: the first arc defines the outer part of the dimple and the second arc defines the central part of the profile. The radii are typically larger in the center, which produces a saucer shaped dimple where the steepness of the walls (and, thus, the edge angle) may be varied independently of the dimple depth and diameter. While effective, this profile is described by a number of equations that at least require first order continuity for tangency between the arcs, as well as varying dimple diameter and depth values to achieve the desired dimple shape.

In addition to the profiles discussed above, dimple patterns have been employed in an effort to control and/or adjust the aerodynamic forces acting on a golf ball. For example, U.S. Pat. Nos. 6,213,898 and 6,290,615 disclose golf ball dimple patterns that reduce high-speed drag and increase low speed lift. It has now been discovered, however, contrary to the disclosures of these patents, that reduced high-speed drag and increased low speed lift does not necessarily result in improved flight performance. For example, excessive high-speed lift or excessive low-speed drag may result in undesirable flight performance characteristics. The prior art is silent, however, as to aerodynamic features that influence other aspects of golf ball flight, such as flight consistency, as well as enhanced aerodynamic coefficients for balls of varying size and weight.

Thus, there remains a need to optimize the aerodynamics of a golf ball to improve flight distance and consistency. Further, there is a need to develop dimple arrangements and profiles that result in longer distance and more consistent flights regardless of the swing-speed of a player, the orientation of the ball when impacted, or the physical properties of the ball

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being played. The use of catenary dimple profiles is considered one way to achieve these objectives.

SUMMARY OF THE INVENTION

The present invention is directed to a golf ball having a plurality of recessed dimples on the surface thereof, wherein at least a portion of the plurality of recessed dimples have a profile defined by the revolution of a catenary curve according to the following function:

$$y = \frac{d_c (\cosh(sf * x) - 1)}{\cosh(sf * \frac{D}{2}) - 1}$$

wherein y is the vertical direction coordinate away from the center of the ball with 0 at the center of the dimple;

x is the horizontal (radial) direction coordinate from the dimple apex to the dimple surface with 0 at the center of the dimple;

sf is a shape factor;

d_c is the chordal depth of the dimple; and

D is the diameter of the dimple.

In one embodiment, about 50 percent or more of the dimples on the golf ball are defined by the catenary curve expression above. In another embodiment, about 80 percent or more of the dimples on the golf ball are defined by the catenary curve expression. In this aspect of the invention, D may range from about 0.100 inches to about 0.225 inches, sf from about 5 to about 200, and d_c from about 0.002 inches to about 0.008 inches. For example, D may be from about 0.115 inches to about 0.185 inches, sf from about 10 to about 100 or from about 10 to about 75, and d_c from about 0.004 inches to about 0.006 inches. In one embodiment, D is from about 0.115 inches to about 0.185 inches, sf is from about 10 to 100, and d_c is from about 0.004 inches to about 0.006 inches.

The golf ball may also include a plurality of dimples having an aerodynamic coefficient magnitude defined by $C_{mag} = \sqrt{(C_L^2 + C_D^2)}$ and an aerodynamic force angle defined by $\text{Angle} = \tan^{-1}(C_L/C_D)$, wherein C_L is a lift coefficient and C_D is a drag coefficient, wherein the golf ball includes: a first aerodynamic coefficient magnitude between about 0.24 and about 0.29 and a first aerodynamic force angle between about 32 degrees and about 39 degrees at a Reynolds Number of about 230000 and a spin ratio of about 0.080; and a second aerodynamic coefficient magnitude between about 0.24 and about 0.29 and a second aerodynamic force angle between about 33 degrees and about 41 degrees at a Reynolds Number of about 208000 and a spin ratio of about 0.090.

In this regard, the golf ball may also include a third aerodynamic coefficient magnitude between about 0.25 and about 0.30 and a third aerodynamic force angle between about 34 degrees and about 42 degrees at a Reynolds Number of about 190000 and a spin ratio of about 0.10; and a fourth aerodynamic coefficient magnitude between about 0.25 and about 0.31 and a fourth aerodynamic force angle between about 35 degrees and about 43 degrees at a Reynolds Number of about 170000 and a spin ratio of about 0.11.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other aspects of the present invention may be more fully understood with reference to, but not limited by, the following drawings.

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FIG. 1 is an illustration of the forces acting on a golf ball in flight;

FIG. 2 is an illustration of the air flow around a golf ball in flight;

FIG. 3 is a graphical interpretation of a catenary curve with different values of the parameter a .

FIG. 4 shows a method for measuring the depth, diameter (twice the radius), and edge angle of a dimple;

FIG. 5 is a dimple cross-sectional profile defined by a hyperbolic cosine function, cosh, with a shape constant of 20, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.51;

FIG. 6 is a dimple cross-sectional profile defined by a hyperbolic cosine function, cosh, with a shape constant of 40, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.55;

FIG. 7 is a dimple cross-sectional profile defined by a hyperbolic cosine function, cosh, with a shape constant of 60, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.60;

FIG. 8 is a dimple cross-sectional profile defined by a hyperbolic cosine function, cosh, with a shape constant of 80, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.64;

FIG. 9 is a dimple cross-sectional profile defined by a hyperbolic cosine function, cosh, with a shape constant of 100, a dimple depth of 0.025 inches, a dimple radius of 0.05 inches, and a volume ratio of 0.69;

FIG. 10 illustrates dimple cross-sectional profiles that are defined by a hyperbolic cosine function, cosh, with varying shape constants, a dimple diameter of 0.150 inches, and a dimple chordal depth of 0.006 inches;

FIG. 11 illustrates dimple cross-sectional profiles that are defined by a hyperbolic cosine function, cosh, with varying dimple diameters, a shape factor of 100, and a dimple chordal depth of 0.006 inches;

FIG. 12 illustrates dimple cross-sectional profiles that are defined by a hyperbolic cosine function, cosh, with varying dimple chordal depths, a shape factor of 100, and a dimple diameter of 0.150 inches;

FIG. 13 is an isometric view of the icosahedron pattern used on a golf ball;

FIG. 14 is an isometric view of the icosahedron pattern used on a golf ball showing the triangular regions formed by the icosahedron pattern;

FIG. 15 is an isometric view of a golf ball according to the present invention having an icosahedron pattern, showing dimple sizes;

FIG. 16 is a top view of the golf ball in FIG. 15, showing dimple sizes and arrangement;

FIG. 17 is an isometric view of another embodiment of a golf ball according to the present invention having an icosahedron pattern, showing dimple sizes and the triangular regions formed from the icosahedron pattern;

FIG. 18 is a top view of the golf ball in FIG. 17, showing dimple sizes and arrangement;

FIG. 19 is a top view of the golf ball in FIG. 17, showing dimple arrangement;

FIG. 20 is a side view of the golf ball in FIG. 17, showing the dimple arrangement at the equator;

FIG. 21 is a spherical-triangular region of a golf ball according to the present invention having an octahedral dimple pattern, showing dimple sizes;

FIG. 22 is the spherical triangular region of FIG. 21, showing the triangular dimple arrangement;

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FIG. 23 is a graph of the magnitude of aerodynamic coefficients versus Reynolds Number for a golf ball made according to the present invention and a prior art golf ball;

FIG. 24 is a graph of the angle of aerodynamic force versus Reynolds Number for a golf ball made according to the present invention and a prior art golf ball; and

FIG. 25 is a graph illustrating the coordinate system in a dimple pattern according to one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to golf balls having improved aerodynamic performance due, at least in part, to the selection of dimple arrangements and dimple profiles. In particular, the present invention is directed to a golf ball that includes at least a portion of its dimples that are defined by the revolution of a catenary curve about an axis.

The dimple profiles of the present invention may be used with practically any type of ball construction. For instance, the golf ball may have a two-piece design, a double cover, or veneer cover construction depending on the type of performance desired of the ball. Other suitable golf ball constructions include solid, wound, liquid-filled, and/or dual cores, and multiple intermediate layers. Examples of these and other types of ball constructions that may be used with the present invention include those described in U.S. Pat. Nos. 5,713,801, 5,803,831, 5,885,172, 5,919,100, 5,965,669, 5,981,654, 5,981,658, and 6,149,535, as well as in Publication No. US2001/0009310 A1.

Different materials may be used in the construction of the golf balls made with the present invention. For example, the cover of the ball may be made of a thermoset or thermoplastic, a castable or non-castable polyurethane and polyurea, an ionomer resin, balata, or any other suitable cover material known to those skilled in the art. Conventional and non-conventional materials may be used for forming core and intermediate layers of the ball including polybutadiene and other rubber-based core formulations, ionomer resins, highly neutralized polymers, and the like.

After selecting the desired ball construction, the flight performance of the golf ball can be adjusted according to the design, placement, and number of dimples on the ball. As explained in greater detail below, the use of catenary curves provides a relatively effective way to modify the ball flight performance without significantly altering the dimple pattern and, thus, allow greater flexibility to ball designers to better customize a golf ball to suit a player.

Dimple Profiles of the Invention

A catenary curve represents the assumed shape of a perfectly flexible, uniformly dense, and inextensible chain suspended from its endpoints. In general, the mathematical formula representing such a curve is expressed as equation (1):

$$y = a \cosh\left(\frac{x}{a}\right) \quad (1)$$

where a is a constant in terms of horizontal tension in the chain and its weight per unit length, y is the vertical axis and x is the horizontal axis in a two dimensional Cartesian space. The chain is steepest near the points of suspension because this part of the chain has the most weight pulling down on it. Toward the bottom, the slope of the chain decreases because the chain is supporting less weight. FIG. 3 generally demonstrates the concept of a catenary curve with different values of the parameter a .

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The present invention is directed to defining dimples on a golf ball by revolving a catenary curve about its y axis. In particular, the catenary curve used to define a golf ball dimple is a hyperbolic cosine function in the form of:

$$y = \frac{d_c(\cosh(sf * x) - 1)}{\cosh\left(sf * \frac{D}{2}\right) - 1} \quad (2)$$

where: y is the vertical direction coordinate with 0 at the bottom of the dimple and positive upward (away from the center of the ball);

x is the horizontal (radial) direction coordinate, with 0 at the center of the dimple

sf is a shape constant (also called shape factor);

d_c is the chordal depth of the dimple; and

D is the diameter of the dimple.

Unlike the dual radius dimple profile discussed previously, the inventive dimple profiles based on catenary curves are defined by a single continuous, differentiable function having independent variables of dimple diameter, depth, and shape factor (relative curvature and edge angle). Thus, the dimple profiles of the present invention can have any combination of diameter, depth, and edge angle with no additional requirements on derivatives of the function used to define the dimple profile.

The “shape constant” or “shape factor”, sf, is an independent variable in the mathematical expressions described above for a catenary curve. The use of a shape factor in the present invention provides an expedient method of generating alternative dimple profiles, for dimples with fixed radii and depth. For example, the shape factor may be used to independently alter the volume ratio (V_r) of the dimple while holding the dimple depth and radius fixed. The volume ratio is the ratio of the chordal dimple volume (bounded by the dimple surface and its chord plane divided by the volume of a cylinder defined by a similar diameter and chordal depth as the dimple). Accordingly, if a golf ball designer desires to generate balls with alternative lift and drag characteristics for a particular dimple position, diameter, and depth, then the golf ball designer may simply describe alternative shape factors to obtain alternative lift and drag performance without having to change these other parameters. No modification to the dimple layout on the surface of the ball is required.

Similar changes in the volume ratio and aerodynamic performance may be accomplished by using alternate forms of the equation (2) above to define the catenary dimple profile, see, e.g., equations (5), (6), (7), and (8) below.

While the present invention is directed toward using a catenary curve for at least a portion of the dimples on a golf ball, it is not necessary that catenary curves be used on every dimple on a golf ball. In some cases, the use of a catenary curve may only be used for a small number of dimples. Alternatively, a large amount of dimples may have profiles based on a catenary curve. In general, it is preferred that a sufficient number of dimples on the ball have catenary curves so that variation of shape factors will allow a designer to alter the flight characteristics of the ball. Thus, in one embodiment, at least about 30 percent, preferably about 50 percent, and more preferably at least about 60 percent, of the dimples on a golf ball are defined by a catenary curve.

Accordingly, the present invention uses variations of equation (2) to define the cross-section of at least a portion of the dimples on a golf ball. For example, the catenary curve can be defined by hyperbolic sine or cosine functions, ratios of these

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functions or combinations of them. A hyperbolic sine function is defined by the following expression:

$$\sinh(x) = \frac{e^x - e^{-x}}{2} \quad (3)$$

while a hyperbolic cosine function is defined by the following expression:

$$\cosh(x) = \frac{e^x + e^{-x}}{2}. \quad (4)$$

In one embodiment of the present invention, the mathematical equation for describing the cross-sectional profile of a dimple is expressed using the above expression by the following formula:

$$y = \frac{d_c(e^{(sf^2)} + e^{-(sf^2)} - 2)}{e^{(sf \frac{D}{2})} + e^{-(sf \frac{D}{2})} - 2} \quad (5)$$

where: y is the vertical direction coordinate with 0 at the bottom of the dimple and positive upward (away from the center of the ball);

x is the horizontal (radial) direction coordinate, with 0 at the center of the dimple;

sf is a shape factor;

d_c is the chordal depth of the dimple; and

D is the diameter of the dimple.

An alternate embodiment of the present invention involves a mathematical expression in terms of hyperbolic sine using the following formula:

$$y = \frac{d_c(\sqrt{1 + \sinh^2(sf * x)} - 1)}{\sqrt{1 + \sinh^2\left(sf * \frac{D}{2}\right)} - 1} \quad (6)$$

where y, x, sf, d_c, and D are defined as shown above.

In another embodiment of the present invention, a mathematical expression is shown as terms of a series expansion of one of the previous embodiments. However, the formula is preferably restricted to small values of sf, e.g., where sf is less than or equal to about 50. The equation describing the cross-sectional profile is expressed by the following formula:

$$y = \frac{d_c sf^2}{2(\cosh(sf \frac{D}{2}) - 1)} * x^2 + \frac{d_c sf^4}{24(\cosh(sf \frac{D}{2}) - 1)} * x^4 \quad (7)$$

Again y, x, sf, d_c, and D are defined as shown above.

The depth (d_c) and diameter (D) of the dimple may be measured as shown in FIG. 4.

It is understood that, based on the equations and disclosure herein, one skilled in the art would be able to derive other expressions illustrating catenary dimple profiles relating diameter, chord or surface depth, and shape factor. Therefore, the present invention is not limited to the example equations

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discussed above; rather, the present invention encompasses other expressions illustrating catenary dimple profiles relating diameter, chord or surface depth, and shape factor.

In yet another embodiment of the present invention, the mathematical equation for describing the cross-sectional profile of a dimple is expressed by the following formula:

$$y = \frac{d_c(\cosh(sf * x) - 1)}{\cosh(sf * r) - 1} \quad (8)$$

where: y is the vertical direction coordinate with 0 at the bottom of the dimple and positive

upward (away from the center of the ball);

x is the horizontal (radial) direction coordinate, with 0 at the center of the dimple;

sf is a shape constant (also called shape factor);

d is the depth of the dimple from the phantom ball surface; and

r is the radius of the dimple.

The depth (d) and radius (r) ($r = \frac{1}{2}$ diameter (D)) of the dimple may be measured as described in U.S. Pat. No. 4,729, 861 (shown in FIG. 4), the disclosure of which is incorporated by reference in its entirety. The depth (d) is measured from point J to point K on the ball phantom surface 41, and the diameter (D) is measured between the dimple edge points E and F. Although FIG. 4 is meant to depict a dimple of conventional spherical shape, the described methods for measuring dimple dimensions are also applicable to the dimples of the present invention.

Some of the differences between equations (2) and (8) include the use of a) the chordal depth (d_c) in equation (2) as opposed to the depth from phantom surface d in equation (8) and b) the diameter D in equation (2) as opposed to the radius r in equation (8). Referring once again to FIG. 4, the chordal depth (d_c) is measured from point J to the chord line 162.

In addition, another difference between equations (2) and (8) is that computed volume ratios (V_r) will be different. For example, the volume ratios according to equation (8) will always be less than those computed for dimple profiles based on equation (2). However, it will be appreciated by those of ordinary skill in the art that the differences in the computed volume ratios based on the two equations are also dependent on the manner in which volume ratio is computed. In particular, if volume ratio is calculated as the ratio of total dimple volume to a cylinder based on surface depth, then volume ratio will vary for any changes in diameter, chordal depth, and shape factor. On the other hand, if volume ratio is the ratio of dimple volume (up to the chord plane) to a cylinder based on chord depth, then the volume ratio will vary only with changes in diameter and shape factor. Regardless, the greatest differences in volume ratio when using equations (2) and (8) occur as diameter and shape factor increase and chordal depth decreases.

For the equations provided above, and more specifically equation (8), shape constant values that are larger than 1 result in dimple volume ratios greater than 0.5. Preferably, shape factors are between about 20 to about 100. FIGS. 5-9 illustrate dimple profiles for shape factors of 20, 40, 60, 80, and 100, respectively, generated using equation (8). Table 1 illustrates how the volume ratio changes for a dimple with a radius of 0.05 inches and a depth of 0.025 inches.

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TABLE 1

Shape Factor	Volume Ratio
20	0.51
40	0.55
60	0.60
80	0.64
100	0.69

As shown above, increases in shape factor result in higher volume ratios for a given dimple radius and depth.

In this regard, dimple patterns that include dimple profiles based on equation (8) may be at least partially driven by a desired percentage of dimples in the pattern that have a certain volume ratio. For example, one pattern may include about 50 percent or more dimples with a volume ratio of about 0.50 or greater. In one embodiment, about 50 percent to about 80 percent of the dimples have a volume ratio of about 0.5 to about 0.60 and about 20 percent to about 50 percent have a volume ratio of about 0.64 or greater.

In contrast, many different but related shapes of dimples can be generated by manipulating the parameters of equation (2) and other expressions illustrating catenary dimple profiles relating diameter, chord or surface depth, and shape factor. For example, FIG. 10 shows catenary dimple profiles with varying shape factors (diameter and chordal depth are held constant). Table 3 illustrates the increase in volume ratio as shape factor increases from 50 to 150. In particular, an increase in shape factor from 50 to 150 results in an increase in volume ratio of about 133 percent.

TABLE 2

Shape Factor	Diameter (in.)	Chordal Depth (in.)	Volume Ratio
50	0.15	0.006	0.63
100			0.77
150			0.84

In addition, while not exactly correlative due to the differences between equations (2) and (8), the larger diameters and shallower depth used in FIG. 10 and Table 2 appear to increase the volume ratio. For example, when applied to equation (8), a shape factor of 100, a radius of 0.05 inches, and a depth of 0.025 inches results in a volume ratio of 0.69, whereas the same shape factor with a larger diameter, but shallower dimple profile based on equation (2) results in a volume ratio of 0.77. This is an example of one of number of differences between equations (2) and (8), i.e., the volume ratios computed for dimple profiles according to equation (2) are larger than the volume ratios computed for dimple profiles according to equation (8).

FIG. 11 shows catenary dimple profiles with varying diameters (shape factor and chordal depth are held constant). Table 3 illustrates the increase in volume ratio with a corresponding increase in dimple diameter from 0.120 inches to 0.170 inches.

TABLE 3

Diameter (in.)	Shape Factor	Chordal Depth (in.)	Volume Ratio
0.120	100	0.006	0.72
0.150			0.77
0.170			0.79

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Again, when comparing this result to the results above for equation (8), a larger diameter, shallower dimple profile results in a larger volume ratio at a shape factor of 100.

In this aspect of the invention, when chordal depth is varied and shape factor and diameter is held constant (the diameter is still larger than previously used in equation (8), a larger volume ratio can be obtained when compared to the smaller, deeper dimples used above in equation (8). In particular, FIG. 12 and Table 4 illustrate that, with chordal depth ranging from 0.003 inches to 0.009 inches while the shape factor is held constant at 100 and the diameter is held constant at 0.15 inches, the volume ratio does not change, but it remains larger than the results shown in FIG. 10 and Table 1.

TABLE 4

Chordal Depth (in.)	Shape Factor	Diameter (in.)	Volume Ratio
0.003	100	0.150	0.77
0.006			0.77
0.009			0.77

Without being bound to any particular theory, it is believed that, when used with specific dimple counts, combinations of these three parameters produce optimal flight performance. In particular, specific ranges or combinations of dimple count, diameter, shape factor, and chordal depth (in accordance with equation (2)) are believed to produce optimal flight performance. For example, the number of dimples may range from about 250 to about 500. In one embodiment, the dimple count is from about 250 to about 450. In another embodiment, the dimple count is from about 250 to about 400. In still another embodiment, the number of dimples ranges from about 250 to about 350.

The diameter of the dimples may range from about 0.100 inches to about 0.225 inches. In one embodiment, the dimple diameter ranges from about 0.115 inches to about 0.200 inches. In another embodiment, the dimple diameter ranges from about 0.115 inches to about 0.185 inches. In yet another embodiment, the dimple diameter ranges from about 0.125 inches to about 0.185 inches.

As discussed briefly above, the use of a shape factor, in tandem with a cross-sectional profile based on the revolution of catenary curve according to equations (2) and (5)-(8), facilitate optimization of the flight profile of specific ball designs. As such, the shape factor may range from about 5 to about 200. In one embodiment, the shape factor ranges from about 10 to about 100. In another embodiment, the shape factor ranges from about 10 to about 75. In still another embodiment, the shape factor ranges from about 40 to about 150. In yet another embodiment, the shape factor is at least about 50.

The chordal depth of the dimple may range from about 0.002 inches to about 0.010 inches, preferably about 0.002 inches to about 0.008 inches. In one embodiment, the chordal depth is about 0.003 inches to about 0.009 inches. In another embodiment, the chordal depth is about 0.004 inches to about 0.006 inches.

It is clear from the tables above and associated figures that, when the dimple profile is based on equation (2), the volume ratio changes with changes in diameter and shape factor. In fact, as discussed previously, the volume ratio calculated for dimple profiles according to equation (2) will be larger than the volume ratio calculated for dimple profiles according to equation (8). In particular, shallow, large diameter dimples with profiles based on equation (2) results in a larger volume

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ratio as compared with dimples having more substantive depth and smaller diameters such as those based on equation (8) above.

Dimple profiles based on equation (2) with dimple diameters between about 0.100 inches and about 0.225 inches (or any range therebetween) and chordal depths between about 0.002 inches to about 0.008 inches (or any range therebetween) preferably have volume ratios at least about 0.60 or greater. In one embodiment, the volume ratio is about 0.63 or greater.

In another embodiment, the volume ratio is about 0.070 or greater. In still another embodiment, the volume ratio is about 0.72 or greater. For example, the volume ratio may be between about 0.63 to about 0.84.

In one embodiment, at least 50 percent of the dimples on the golf ball have a dimple profile based on equation (2). In another embodiment, at least about 80 percent of the dimples are based on equation (2). In still another embodiment, at least about 90 percent of the dimples are based on equation (2). In yet another embodiment, 100 percent of the dimples have a dimple profile according to equation (2).

Within these constraints, a portion of this percentage may be based on equation (2) with a fixed chordal depth and shape factor and varying diameters. For example, about 50 percent or more of the dimples having a dimple profile based on equation (2) may have a fixed chordal depth and shape factor and a varying diameter. In one embodiment, the diameter may range from about 0.100 to about 0.225, preferably about 0.115 inches to about 0.200 inches, more preferably about 0.115 inches to about 0.185 inches, and even more preferably about 0.125 inches to about 0.185 inches while the shape factor is constant and from about 5 to about 200, preferably about 10 to about 100, more preferably about 10 to about 75 and the chordal depth is constant and from about 0.002 inches to about 0.008 inches, preferably about 0.003 inches to about 0.006 inches, and more preferably about 0.004 inches to about 0.006 inches. The remaining dimples within the percentage of the dimples on the ball having a profile according to equation (2) may have varying chordal depth and/or shape factor within these ranges and a fixed diameter within the range of 0.100 inches to about 0.225 inches, preferably about 0.115 inches to about 0.200 inches, more preferably about 0.115 inches to about 0.185 inches, and even more preferably about 0.125 inches to about 0.185 inches.

One dimple pattern according to the invention has about 50 percent to about 100 percent of its dimples based on equation (2) with a varying diameter within the range of 0.125 inches to about 0.185 inches and a fixed chordal depth of about 0.004 inches to about 0.006 inches and a fixed shape factor between about 10 to about 75. If less than 100 percent of the dimples are based on equation (2), the remainder of the dimples may have cross-sectional profiles based on parabolic curves, ellipses, semi-spherical curves, saucer-shapes, sine curves, truncated cones, flattened trapezoids, or catenary curves according to equation (2) and/or equations (5)-(8).

For example, dimple patterns according to the present invention may be formed using a combination of equations (2) and (8). For example, in one embodiment, at least a portion of the dimples have a profile based on equation (2) and the remaining portion have dimple profiles based equation (8). In this aspect, about 5 percent to about 40 percent have dimple profiles based on equation (8) and about 60 percent to about 95 percent have dimple profiles based on equation (2). In another embodiment, about 5 percent to about 20 percent have dimple profiles based on equation (8) and about 80 percent to about 95 percent have dimple profiles based on equation (2).

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The portion of the dimples having profiles based on equation (8) has a fixed radius and surface depth of 0.05 to about 0.09 inches and 0.005 to about 0.025 inches, respectively, with varying shape factors. For example, the shape factor may vary from 20 to 100. In one embodiment, the shape factor is at least about 40, but may vary up to 100. In fact, within the percentage of dimples having profiles based on equation (8), preferably about 50 percent or more have a shape factor of 50 or greater. While two or more shape factors may be used for dimples on a golf ball, it is preferred that the differences between the shape factors be relatively similar in order to achieve optimum ball flight performance that corresponds to a particular ball construction and player swing speed. In particular, a plurality of shape factors used to define dimples having catenary curves preferably do not differ by more than 30, and even more preferably do not differ by more than 15.

In this same scenario, the portion of the dimples based on equation (2) may have varying diameter, chordal depth, and shape factor. For example, within the percentage of dimples having a profile based on equation (2), at least 50 percent may have a fixed chordal depth and shape factor with a diameter ranging from about 0.100 to about 0.225, preferably about 0.115 inches to about 0.200 inches, more preferably about 0.115 inches to about 0.185 inches, and even more preferably about 0.125 inches to about 0.185 inches, while the remaining portion of these dimples are a mix of dimple profiles based on equation (2) holding diameter constant, while varying either the shape factor or chordal depth. In one embodiment, about 50 percent to about 80 percent of the dimples having a dimple profile based on equation (2) have a fixed chordal depth and shape factor with varying diameter and about 20 percent to about 50 percent are a mix of varying chordal depth with fixed diameter and fixed shape factor and varying shape factor with fixed diameter and chordal depth.

The use of a dimple shape factor in the catenary curve profiles of the present invention helps to yield particular optimal flight performance for specific swing speed categories. Again, the advantageous feature of shape factor is that dimple location need not be manipulated for each swing speed; only the dimple shape will be altered. Thus, a "family" of golf balls may have a similar general appearance although the dimple shape for at least a portion of the dimples on the ball is altered to optimize flight characteristics for particular swing speeds. Table 5 identifies certain beneficial shape factors for varying swing speeds, i.e., from 155-175 mph, from 140 to 155 mph, and from 125 to 140 mph, cover hardness, and ball compression.

TABLE 5

Ball Design	Dimple Shape Factor	Ball Speed from driver (mph)	Cover Hardness (Shore D)	Ball Compression (Atti)
1	80	155-175	45-55	60-75
2	90	155-175	45-55	75-90
3	100	155-175	45-55	90-105
4	70	155-175	55-65	60-75
5	80	155-175	55-65	75-90
6	90	155-175	55-65	90-105
7	55	155-175	65-75	60-75
8	65	155-175	65-75	75-90
9	75	155-175	65-75	90-105
10	65	140-155	45-55	60-75
11	75	140-155	45-55	75-90
12	85	140-155	45-55	90-105
13	55	140-155	55-65	60-75
14	65	140-155	55-65	75-90
15	75	140-155	55-65	90-105
16	40	140-155	65-75	60-75

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TABLE 5-continued

Ball Design	Dimple Shape Factor	Ball Speed from driver (mph)	Cover Hardness (Shore D)	Ball Compression (Atti)
17	50	140-155	65-75	75-90
18	60	140-155	65-75	90-105
19	50	125-140	45-55	60-75
20	60	125-140	45-55	75-90
21	70	125-140	45-55	90-105
22	40	125-140	55-65	60-75
23	50	125-140	55-65	75-90
24	60	125-140	55-65	90-105
25	25	125-140	65-75	60-75
26	35	125-140	65-75	75-90
27	45	125-140	65-75	90-105

To illustrate the selection of shape factors in dimple design from Table 5, the preferred dimple shape factor for a ball having a cover hardness of about 45 to about 55 Shore D and a ball compression of about 60 to about 75 Atti for a player with a ball speed from the driver between about 140 and about 155 mph would be about 65. Likewise, the preferred shape factor for the same ball construction, but for a player having a ball speed from the driver of between about 155 mph and about 175 mph would be about 80. As mentioned above, these preferred shape factors may be adjusted upwards or downwards by 20, 10, or 5 to arrive at a further customized ball design.

Table 5 shows that as the spin rate and ball speed off the driver increase, the shape factor should also increase to provide optimal aerodynamic performance, e.g., increased flight distance. While the shape factors listed above illustrate preferred embodiments for varying ball constructions and ball speeds, the shape factors listed above for each example may be varied without departing from the spirit and scope of the present invention. For example, in one embodiment, the shape factors listed for each example above may be adjusted upwards or downwards by 20 to arrive at a further customized ball design. More preferably, the shape factors may be adjusted upwards or downwards by 10, and even more preferably it may be adjusted by 5.

Thus, shape factors may be selected for a particular ball construction that result in a ball designed to work well with a wide variety of player swing speeds. For instance, in one embodiment of the present invention, a shape factor between about 65 and about 100 would be suitable for a ball with a cover hardness between about 45 and about 55 shore D.

As such, not only do the preferred ranges of dimple radius and/or diameter, depth, and shape factor discussed above with respect to equations (2) and (8) factor into the design of a dimple profile and overall dimple pattern, the player swing speed will also likely play a role. In this regard, the range of shape factors for dimple profiles based on equations (2) or (8) may be adjusted to cater to a certain player swing speed. For example, while a preferred shape factor range is from about 10 to about 75, this may be adjusted depending on the targeted player swing speed and ball construction.

Dimple Patterns

Dimple patterns that provide a high percentage of surface coverage are preferred, and are well known in the art. For example, U.S. Pat. Nos. 5,562,552, 5,575,477, 5,957,787, 5,249,804, and 4,925,193 disclose geometric patterns for positioning dimples on a golf ball.

In one embodiment of the present invention, the dimple pattern is at least partially defined by phyllotaxis-based pat-

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terns, such as those described in copending U.S. Pat. No. 6,338,684, the entire disclosure of which is incorporated by reference in its entirety.

In one embodiment, the selected dimple pattern provides greater than about 50 percent surface coverage. In another embodiment, about 70 percent or more of the golf ball surface is covered by dimples. In yet another embodiment, about 80 percent or more of the golf ball surface is covered by dimples. In still another embodiment, about 90 percent or more of the golf ball surface is covered by dimples. Various patterns with varying levels of coverage are discussed below. Any of these patterns or modification to these patterns are contemplated for use in accordance with the present invention.

FIGS. 13 and 14 show a golf ball 10 with a plurality of dimples 11 on the outer surface that are formed into a dimple pattern having two sizes of dimples. The first set of dimples A have diameters of about 0.14 inches and form the outer triangle 12 of the icosahedron dimple pattern. The second set of dimples B have diameters of about 0.16 inches and form the inner triangle 13 and the center dimple 14. The dimples 11 cover less than 80 percent of the outer surface of the golf ball and there is a significant number of large spaces 15 between adjacent dimples, i.e., spaces that could hold a dimple of 0.03 inches diameter or greater.

FIGS. 15 and 16 show a golf ball 20 according to the first dimple pattern embodiment of the present invention with a plurality of dimples 21 in an icosahedron pattern. In an icosahedron pattern, there are twenty triangular regions that are generally formed from the dimples. The icosahedron pattern has five triangles formed at both the top and bottom of the ball, each of which shares the pole dimple as a point. There are also ten triangles that extend around the middle of the ball.

In this first dimple pattern embodiment, there are five different sized dimples A-E, wherein dimples E (D_E) are greater than dimples D (D_D), which are greater than dimples C (D_C), which are greater than dimples B (D_B), which are greater than dimples A (D_A); $D_E > D_D > D_C > D_B > D_A$. Dimple minimum sizes according to this embodiment are set forth in Table 6 below:

TABLE 6

Dimple Sizes for Suitable Dimple Pattern	
Dimple	Percent of Ball Diameter
A	6.55
B	8.33
C	9.52
D	10.12
E	10.71

The dimples of this embodiment are formed in large triangles 22 and small triangles 23. The dimples along the sides of the large triangle 22 increase in diameter toward the midpoint 24 of the sides. The largest dimple along the sides, D_E , is located at the midpoint 24 of each side of the large triangle 22, and the smallest dimples, D_A , are located at the triangle points 25. In this embodiment, each dimple along the sides is larger than the adjacent dimple toward the triangle point.

FIGS. 17-20 illustrate another suitable dimple pattern contemplated for use on the golf ball of the present invention. In this embodiment, there are again five different sized dimples A-E, wherein dimples E (D_E) are greater than dimples D (D_D), which are greater than dimples C (D_C), which are greater than dimples B (D_B), which are greater than dimples A (D_A); $D_E > D_D > D_C > D_B > D_A$. Dimple minimum sizes according to this embodiment are set forth in Table 7 below:

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TABLE 7

Dimple Sizes for Suitable Dimple Pattern	
Dimple	Percent of Ball Diameter
A	6.55
B	8.93
C	9.23
D	9.52
E	10.12

In this dimple pattern, the dimples are again formed in large triangles 22 and small triangles 23 as shown in FIG. 19. The dimples along the sides of the large triangle 22 increase in diameter toward the midpoint 24 of the sides. The largest dimple along the sides, D_D , is located at the midpoint 24 of each side of the large triangle 22, and the smallest dimples, D_A , are located at the triangle points 25. In this embodiment, each dimple along the sides is larger than the adjacent dimple toward the triangle point, i.e., $D_B > D_A$ and $D_D > D_B$.

Another suitable dimple pattern embodiment is illustrated in FIGS. 21-22, wherein the golf ball has an octahedral dimple pattern. In an octahedral dimple pattern, there are eight spherical triangular regions 30 that form the ball. In this dimple pattern, there are six different sized dimples A-F, wherein dimples F (D_F) are greater than dimples E (D_E), which are greater than dimples D (D_D), which are greater than dimples C (D_C), which are greater than dimples B (D_B), which are greater than dimples A (D_A); $D_F > D_E > D_D > D_C > D_B > D_A$. Dimple minimum sizes according to this embodiment are set forth in Table 8 below:

TABLE 8

Dimple Sizes for Suitable Dimple Pattern	
Dimple	Percentage of Ball Diameter
A	5.36
B	6.55
C	8.33
D	9.83
E	9.52
F	10.12

In this dimple pattern embodiment, the dimples are formed in large triangles 31, small triangles 32 and smallest triangles 33. Each dimple along the sides of the large triangle 31 is equal to or larger than the adjacent dimple from the point 34 to the midpoint 35 of the triangle 31. The dimples at the midpoint 35 of the side, D_E , are the largest dimples along the side and the dimples at the points 34 of the triangle, D_A , are the smallest. In addition, each dimple along the sides of the small triangle 32 is also equal to or larger than the adjacent dimple from the point 36 to the midpoint 37 of the triangle 32. The dimple at the midpoint 37 of the side, D_F , is the largest dimple along the side and the dimples at the points 36 of the triangle, D_C , are the smallest.

Dimple Packing

In one embodiment, the golf balls of the invention include an icosahedron dimple pattern, wherein each of the sides of the large triangles is formed from an odd number of dimples and each of the side of the small triangles are formed with an even number of dimples.

For example, in the icosahedron pattern shown in FIGS. 15-16 and 17-20, there are seven dimples along each of the

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sides of the large triangle 22 and four dimples along each of the sides of the small triangle 23. Thus, the large triangle 22 has nine more dimples than the small triangle 23, which creates hexagonal packing 26, i.e., each dimple is surrounded by six other dimples for most of the dimples on the ball. For example, the center dimple, D_E , is surrounded by six dimples slightly smaller, D_D . In one embodiment, at least 75 percent of the dimples have 6 adjacent dimples. In another embodiment, only the dimples forming the points of the large triangle 25, D_A , do not have hexagonal packing. Since D_A are smaller than the adjacent dimples, the gaps between adjacent dimples is surprisingly small when compared to the golf ball shown in FIG. 15.

The golf ball 20 has a greater dispersion of the largest dimples. For example, in FIG. 15, there are four of the largest diameter dimples, D_E , located in the center of the triangles and at the mid-points of the triangle sides. Thus, there are no two adjacent dimples of the largest diameter. This improves dimple packing and aerodynamic uniformity. Similarly, in FIG. 17, there is only one largest diameter dimple, D_E , which is located in the center of the triangles. Even the next to the largest dimples, D_D , are dispersed at the mid-points of the large triangles such that there are no two adjacent dimples of the two largest diameters, except where extra dimples have been added along the equator.

In the last example dimple pattern discussed above, i.e., FIGS. 21-22, each of the sides of the large triangle 31 has an even number of dimples, each of the sides of the small triangle 32 has an odd number of dimples and each of the sides of the smallest triangle 33 has an even number of dimples. There are ten dimples along the sides of the large triangles 31, seven dimples along the sides of the small triangles 32, and four dimples along the sides of the smallest triangles 33. Thus, the large triangle 31 has nine more dimples than the small triangle 32 and the small triangle 32 has nine more dimples than the smallest triangle 33. This creates the hexagonal packing for all of the dimples inside of the large triangles 31.

As used herein, adjacent dimples can be considered as any two dimples where the two tangent lines from the first dimple that intersect the center of the second dimple do not intersect any other dimple. In one embodiment, less than 30 percent of the gaps between adjacent dimples is greater than 0.01 inches. In another embodiment, less than 15 percent of the gaps between adjacent dimples is greater than 0.01 inches.

As discussed above, one embodiment of the present invention contemplates dimple coverage of greater than about 80 percent. For example, the percentages of surface area covered by dimples in the embodiments shown in FIGS. 15-16 and 17-20 are about 85.7 percent and 82 percent, respectively whereas the ball shown in FIG. 14 has less than 80 percent of its surface covered by dimples. The percentage of surface area covered by dimples as shown in FIGS. 21-22 is also about 82 percent, whereas prior art octahedral balls have less than 77 percent of their surface covered by dimples, and most have less than 60 percent. Thus, there is a significant increase in surface area contemplated for the golf balls of the present invention as compared to prior art golf balls.

Parting Line

A parting line, or annular region, about the equator of a golf ball has been found to separate the flow profile of the air into two distinct halves while the golf ball is in flight and reduce the aerodynamic force associated with pressure recovery, thus improving flight distance and roll. The parting line must coincide with the axis of ball rotation. It is possible to manufacture a golf ball without parting line, however, most balls have one for ease of manufacturing, e.g., buffing of the golf

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balls after molding, and many players prefer to have a parting line to use as an alignment aid for putting.

In one embodiment of the present invention, the golf balls include a dimple pattern containing at least one parting line, or annular region. In another embodiment, there is no parting line that does not intersect any dimples, as illustrated in the golf ball shown in FIG. 15. While this increases the percentage of the outer surface that is covered by dimples, the lack of the parting line may make manufacturing more difficult.

In yet another embodiment, the dimple pattern is such that any dimples adjacent to the parting line are aligned and positioned to overlap across the parting line. In essence, this creates a staggered wave parting line. Examples of such dimple patterns are described in U.S. Pat. Nos. 7,258,632 and 6,969,327 and U.S. Patent Publication No. 2006/0025245, the disclosures of which are incorporated by reference herein.

In yet another embodiment, the parting line(s) may include regions of no dimples or regions of shallow dimples. For example, most icosahedron patterns generally have modified triangles around the mid-section to create a parting line that does not intersect any dimples. Referring specifically to FIG. 20, the golf ball in this embodiment has a modified icosahedron pattern to create the parting line 27, which is accomplished by inserting an extra row of dimples. In the triangular section identified with lettered dimples, there is an extra row 28 of D-C-C-D dimples added below the parting line 27. Thus, the modified icosahedron pattern in this embodiment has thirty more dimples than the unmodified icosahedron pattern in the embodiment shown in FIGS. 15-16.

In another embodiment, there are more than two parting lines that do not intersect any dimples. For example, the octahedral golf ball shown in FIGS. 21-22 contains three parting lines 38 that do not intersect any dimples. This decreases the percentage of the outer surface as compared to the first embodiment, but increases the symmetry of the dimple pattern. In another embodiment, the golf balls according to the present invention may have the dimples arranged so that there are less than four parting lines that do not intersect any dimples.

Aerodynamic Performance

As discussed generally in the background section, dimples play a key role in the lift and drag on a golf ball. The lift and drag forces are computed as follows:

$$F_{lift}=0.5 \rho C_l A V^2 \quad (9)$$

$$F_{drag}=0.5 \rho C_d A V^2 \quad (10)$$

where: ρ =air density

C_l =lift coefficient

C_d =drag coefficient

A =ball area= πr^2 (where r =ball radius), and

V =ball velocity

Lift and drag coefficients are dependent on air density, air viscosity, ball speed, and spin rate and the influence of all of these parameters may be captured by two dimensionless parameters, i.e., Reynolds Number (N_{Re}) and Spin Ratio (SR). Spin Ratio is the rotational surface speed of the ball divided by ball velocity. Reynolds Number quantifies the ratio of inertial to viscous forces acting on the golf ball moving through the air. SR and N_{Re} are calculated in equations (11) and (12) below:

$$SR=\omega(D/2)/N \quad (11)$$

$$N_{Re}=DV\rho/\mu \quad (12)$$

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where ω =ball rotation rate (radians/s) (2π (RPS))

RPS=ball rotation rate (revolution/s)

V=ball velocity (ft/s)

D=ball diameter (ft)

ρ =air density (slugs/ft³)

μ =absolute viscosity of air (lb/ft-s)

There is a number of suitable methods for determining the lift and drag coefficients for a given range of SR and N_{Re} , which include the use of indoor test ranges with ballistic screen technology. U.S. Pat. No. 5,682,230, the entire disclosure of which is incorporated by reference herein, teaches the use of a series of ballistic screens to acquire lift and drag coefficients. U.S. Pat. Nos. 6,186,002 and 6,285,445, also incorporated in their entirety by reference herein, disclose methods for determining lift and drag coefficients for a given range of velocities and spin rates using an indoor test range, wherein the values for C_L and C_D are related to SR and N_{Re} for each shot. One skilled in the art of golf ball aerodynamics testing could readily determine the lift and drag coefficients through the use of an indoor test range.

For a golf ball of any diameter and weight, increased distance is obtained when the lift force, F_{lift} , on the ball is greater than the weight of the ball but preferably less than three times its weight. This may be expressed as:

$$W_{ball} \leq F_{lift} \leq 3W_{ball}$$

The preferred lift coefficient range which ensures maximum flight distance is thus:

$$\frac{2W_{ball}}{\pi^2 \rho V^2} \leq C_L \leq \frac{6W_{ball}}{\pi^2 \rho V^2}$$

The lift coefficients required to increase flight distance for golfers with different ball launch speeds may be computed using the formula provided above. Table 9 provides several examples of the preferred range for lift coefficients for alternative launch speeds, ball size, and weight:

TABLE 9

PREFERRED RANGES FOR LIFT COEFFICIENT FOR A GIVEN BALL DIAMETER, WEIGHT, AND LAUNCH VELOCITY FOR A GOLF BALL ROTATING AT 3000 RPM						
Preferred Minimum C_L	Preferred Maximum C_L	Ball Diameter (in.)	Ball Weight (oz.)	Ball Velocity (ft/s)	Reynolds Number	Spin Ratio
0.09	0.27	1.75	1.8	250	232008	0.092
0.08	0.24	1.75	1.62	250	232008	0.092
0.07	0.21	1.75	1.4	250	232008	0.092
0.10	0.29	1.68	1.8	250	222727	0.088
0.09	0.27	1.68	1.62	250	222727	0.088
0.08	0.23	1.68	1.4	250	222727	0.088
0.12	0.37	1.5	1.8	250	198864	0.079
0.11	0.33	1.5	1.62	250	198864	0.079
0.10	0.29	1.5	1.4	250	198864	0.079
0.14	0.42	1.75	1.8	200	185606	0.115
0.13	0.38	1.75	1.62	200	185606	0.115
0.11	0.33	1.75	1.4	200	185606	0.115
0.15	0.46	1.68	1.8	200	178182	0.110
0.14	0.41	1.68	1.62	200	178182	0.110
0.12	0.36	1.68	1.4	200	178182	0.110
0.19	0.58	1.5	1.8	200	159091	0.098
0.17	0.52	1.5	1.62	200	159091	0.098
0.15	0.45	1.5	1.4	200	159091	0.098

Because of the key role a dimple profile plays in lift and drag on a golf ball, once a dimple pattern is selected for the

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golf ball, the shape factor used in the catenary curve equations may be adjusted to achieve the desired lift coefficient. Effective ways of arriving at the optimal shape factor(s) include wind tunnel testing or using a light gate test range to empirically determine the catenary shape factor that provides the desired lift coefficient at the desired launch velocity. Preferably, the measurement of lift coefficient is performed with the golf ball rotating at typical driver rotation speeds. A preferred spin rate for performing the lift and drag tests is 3,000 rpm.

In addition to selecting particular dimple profiles based on catenary curves, improved flight distance may also be achieved by selecting the dimple pattern and dimple profiles so that specific magnitude and direction criteria are satisfied. In particular, two parameters that account for both lift and drag simultaneously, i.e., 1) the magnitude of aerodynamic force (C_{mag}) and 2) the direction of the aerodynamic force (Angle), are linearly related to the lift and drag coefficients. Therefore, the magnitude and angle of the aerodynamic coefficients may be used as an additional tool to achieve the desired aerodynamic performance of the ball. The magnitude and the angle of the aerodynamic coefficients are defined in equations (13) and (14) below:

$$C_{mag} = \sqrt{(C_L^2 + C_D^2)} \quad (13)$$

$$\text{Angle} = \tan^{-1}(C_L/C_D) \quad (14)$$

Table 10 illustrates the aerodynamic criteria for a golf ball of the present invention that results in increased flight distances. The criteria are specified as low, median, and high C_{mag} and Angle for eight specific combinations of SR and N_{Re} . Golf balls with C_{mag} and Angle values between the low and the high number are preferred. More preferably, the golf balls of the invention have C_{mag} and Angle values between the low and the median numbers delineated in Table 10. The C_{mag} values delineated in Table 10 are intended for golf balls that conform to USGA size and weight regulations. The size and weight of the golf balls used with the aerodynamic criteria of Table 10 are 1.68 inches and 1.62 ounces, respectively.

TABLE 10

Aerodynamic Characteristics Ball Diameter = 1.68 inches, Ball Weight = 1.62 ounces							
Magnitude ¹				Angle ² (°)			
N_{Re}	SR	Low	Median	High	Low	Median	High
230000	0.085	0.24	0.265	0.27	31	33	35
207000	0.095	0.25	0.271	0.28	34	36	38
184000	0.106	0.26	0.280	0.29	35	38	39
161000	0.122	0.27	0.291	0.30	37	40	42
138000	0.142	0.29	0.311	0.32	38	41	43
115000	0.170	0.32	0.344	0.35	40	42	44
92000	0.213	0.36	0.390	0.40	41	43	45
69000	0.284	0.40	0.440	0.45	40	42	44

¹As defined by equation (13)

²As defined by equation (14)

To ensure consistent flight performance regardless of ball orientation, the percent deviation of C_{mag} for each of the SR and N_{Re} combinations listed in Table 10 plays an important role. The percent deviation of C_{mag} may be calculated in accordance with equation (15), wherein the ratio of the absolute value of the difference between the C_{mag} for two orientations to the average of the C_{mag} for the two orientations is multiplied by 100.

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$$\text{Percent deviation } C_{mag} = |C_{mag1} - C_{mag2}| / ((C_{mag1} + C_{mag2}) / 2) * 100 \quad (15)$$

where $C_{mag1} = C_{mag}$ for orientation 1

$C_{mag2} = C_{mag}$ for orientation 2

In one embodiment, the percent deviation is about 6 percent or less. In another embodiment, the deviation of C_{mag} is about 3 percent or less. To achieve the consistent flight performance, the percent deviation criteria of equation (15) is preferably satisfied for each of the eight C_{mag} values associated with the eight SR and N_{Re} values contained in Table 10.

Aerodynamic asymmetry may arise from parting lines that are inherent in the dimple arrangement or from parting lines associated with the manufacturing process. The percent C_{mag} deviation should be obtained using C_{mag} values measured with the axis of rotation normal to the parting line, commonly referred to as a poles horizontal, PH, orientation and C_{mag} values measured in an orientation orthogonal to PH, commonly referred to as a pole over pole, PP orientation. The maximum aerodynamic asymmetry is generally measured between the PP and PH orientation.

One of ordinary skill in the art would be aware, however, that the percent deviation of C_{mag} as outlined above applies to PH and PP, as well as any other two orientations. For example, if a particular dimple pattern is used having a great circle of shallow dimples, which will be described in greater detail below, different orientations should be measured. The axis of rotation to be used for measurement of symmetry in the above example scenario would be normal to the plane described by the great circle and coincident to the plane of the great circle.

It has also been discovered that the C_{mag} and Angle criteria delineated in Table 10 for golf balls with a nominal diameter of 1.68 and a nominal weight of 1.62 ounces may be advantageously scaled to obtain the similar optimized criteria for golf balls of any size and weight. The aerodynamic criteria of Table 10 may be adjusted to obtain the C_{mag} and angle for golf balls of any size and weight in accordance with equations (16) and (17).

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$$C_{mag(ball)} = C_{mag(Table\ 1)} \sqrt{(\sin(\text{Angle}_{(Table\ 1)}) * (W_{ball} / 1.62) * (1.68 / D_{ball}))^2 + (\cos(\text{Angle}_{(Table\ 1)})^2)} \quad (16)$$

$$\text{Angle}_{(ball)} = \tan^{-1}(\tan(\text{Angle}_{(Table\ 1)}) * (W_{ball} / 1.62) * (1.68 / D_{ball}))^2 \quad (17)$$

For example, Table 11 illustrates aerodynamic criteria for balls with a diameter of 1.60 inches and a weight of 1.7 ounces as calculated using Table 10, ball diameter, ball weight, and equations (13) and (14).

TABLE 11

Aerodynamic Characteristics							
Ball Diameter = 1.60 inches, Ball Weight = 1.70 ounces							
N_{Re}	SR	Magnitude ¹			Angle ² (0)		
		Low	Median	High	Low	Median	High
230000	0.085	0.24	0.265	0.27	31	33	35
207000	0.095	0.262	0.287	0.297	38	40	42
184000	0.106	0.271	0.297	0.308	39	42	44
161000	0.122	0.83	0.311	0.322	42	44	46
138000	0.142	0.304	0.333	0.346	43	45	47
115000	0.170	0.337	0.370	0.383	44	46	49
92000	0.213	0.382	0.420	0.435	45	47	50
69000	0.284	0.430	0.473	0.489	44	47	49

¹As defined by equation (13)

²As defined by equation (14)

Table 12 shows lift and drag coefficients (C_L , C_D), as well as C_{mag} and Angle, for a golf ball having a nominal diameter of 1.68 inches and a nominal weight of 1.61 ounces, with an icosahedron pattern with 392 dimples and two dimple diameters, of which the dimple pattern will be described in more detail below. The percent deviation in C_{mag} for PP and PH ball orientations are also shown over the range of N_{Re} and SR. The deviation in C_{mag} for the two orientations over the entire range is less than about 3 percent.

TABLE 12

Aerodynamic Characteristics										
Ball Diameter = 1.68 inches, Ball Weight = 1.61 ounces										
N_{Re}	SR	PP Orientation				PH Orientation				% Dev C_{mag}
		C_L	C_D	C_{mag}^1	Angle ²	C_L	C_D	C_{mag}^1	Angle ²	
230000	0.085	0.144	0.219	0.262	33.4	0.138	0.217	0.257	32.6	1.9
207000	0.095	0.159	0.216	0.268	36.3	0.154	0.214	0.264	35.7	1.8
184000	0.106	0.169	0.220	0.277	37.5	0.166	0.216	0.272	37.5	1.8
161000	0.122	0.185	0.221	0.288	39.8	0.181	0.221	0.286	39.4	0.9
138000	0.142	0.202	0.232	0.308	41.1	0.199	0.233	0.306	40.5	0.5
115000	0.170	0.229	0.252	0.341	42.2	0.228	0.252	0.340	42.2	0.2
92000	0.213	0.264	0.281	0.386	43.2	0.270	0.285	0.393	43.5	1.8
69000	0.284	0.278	0.305	0.413	42.3	0.290	0.309	0.423	43.2	2.5
SUM		2.543				SUM 2.541				

¹As defined by equation (16)

²As defined by equation (17)

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Table 13 shows lift and drag coefficients (C_L , C_D), as well as C_{mag} and Angle for a prior golf ball having a nominal diameter of 1.68 inches and a nominal weight of 1.61 ounces. The percent deviation in C_{mag} for PP and PH ball orientations are also shown over the range of N_{Re} and SR. The deviation in C_{mag} for the two orientations is greater than about 3 percent over the entire range, greater than about 6 percent for N_{Re} of 161000, 138000, 115000, and 92000, and exceeds 10 percent at a N_{Re} of 69000.

TABLE 13

Aerodynamic Characteristics For Prior Art Golf Ball Ball Diameter = 1.68 inches, Ball Weight = 1.61 ounces										
PP Orientation						PH Orientation				
N_{Re}	SR	C_L	C_D	C_{mag}^1	Angle ²	C_L	C_D	C_{mag}^1	Angle ²	% Dev C_{mag}
230000	0.085	0.151	0.222	0.269	34.3	0.138	0.219	0.259	32.3	3.6
207000	0.095	0.160	0.223	0.274	35.6	0.145	0.219	0.263	33.4	4.1
184000	0.106	0.172	0.227	0.285	37.2	0.154	0.221	0.269	34.8	5.6
161000	0.122	0.188	0.233	0.299	38.9	0.166	0.225	0.279	36.5	6.9
138000	0.142	0.209	0.245	0.322	40.5	0.184	0.231	0.295	38.5	8.7
115000	0.170	0.242	0.269	0.361	42.0	0.213	0.249	0.328	40.5	9.7
92000	0.213	0.280	0.309	0.417	42.2	0.253	0.283	0.380	41.8	9.5
69000	0.284	0.270	0.308	0.409	41.2	0.308	0.337	0.457	42.5	10.9
SUM		2.637				SUM		2.531		

¹As defined by equation (16)

²As defined by equation (17)

Table 14 illustrates the flight performance of a golf ball of the present invention having a nominal diameter of 1.68 inches and weight of 1.61 ounces, compared to a prior art golf ball having similar diameter and weight. Each prior art ball is compared to a golf ball of the present invention at the same speed, angle, and back spin.

TABLE 14

Ball Flight Performance, Invention vs. Prior Art Golf Ball Ball Diameter = 1.68 inches, Ball Weight = 1.61 ounces							
	Ball Orientation	Speed (mph)	Angle	Rotation Rate (rpm)	Distance (yds)	Time (s)	Impact Angle
Prior Art	PP	168.4	8.0	3500	267.2	7.06	41.4
	PH	168.4	8.0	3500	271.0	6.77	36.2
Invention	PP	168.4	8.0	3500	276.7	7.14	39.9
	PH	168.4	8.0	3500	277.6	7.14	39.2
Prior Art	PP	145.4	8.0	3000	220.8	5.59	31.3
	PH	145.4	8.0	3000	216.9	5.18	25.4
Invention	PP	145.4	8.0	3000	226.5	5.61	29.3
	PH	145.4	8.0	3000	226.5	5.60	28.7

Table 14 shows an improvement in flight distance for a golf ball of the present invention of between about 6 to about 10 yards over a similar size and weight prior art golf ball. Table 14 also shows that the flight distance of prior art golf balls is dependent on the orientation when struck, i.e., a deviation between a PP and PH orientation results in about 4 yards distance between the two orientations. In contrast, golf balls of the present invention exhibit less than about 1 yard variation in flight distance due to orientation. Additionally, prior art golf balls exhibit large variations in the angle of ball impact with the ground at the end of flight, i.e., about 5°, for

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the two orientations, while golf balls of the present invention have a variation in impact angles for the two orientations of less than about 1°. A large variation in impact angle typically leads to significantly different amounts of roll when the ball strikes the ground.

The advantageously consistent flight performance of a golf ball of the present invention, i.e., the less variation in flight distance and impact angle, results in more accurate play and potentially yields lower golf scores. FIGS. 23 and 24 illustrate

the magnitude of the aerodynamic coefficients and the angle of aerodynamic force plotted versus N_{Re} for a golf ball of the present invention and a prior art golf ball, each having a diameter of about 1.68 inches and a weight of about 1.61 ounces with a fixed spin rate of 3000 rpm. As shown in FIG. 23, the magnitude of the aerodynamic coefficient is substan-

tially lower and more consistent between orientations for a golf ball of the present invention as compared to a prior art golf ball throughout the range of N_{Re} tested. FIG. 24 illustrates that the angle of the aerodynamic force is more consistent for a golf ball of the present invention as compared to a prior art golf ball.

Aerodynamic Symmetry

To create a ball that adheres to the Rules of Golf, as approved by the United States Golf Association, the ball must not be designed, manufactured or intentionally modified to have properties that differ from those of a spherically sym-

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metrical ball. Aerodynamic symmetry allows the ball to fly with little variation no matter how the golf ball is placed on the tee or ground.

As such, the dimple patterns discussed above are preferably selected and/or designed to cover the maximum surface area of the golf ball without detrimentally affecting the aerodynamic symmetry of the golf ball. A representative coordinate system used to model some of the dimple patterns discussed above is shown in FIG. 25. The XY plane is the equator of the ball while the Z direction goes through the pole of the ball. Preferably, the dimple pattern is generated from the equator of the golf ball, the XY plane, to the pole of the golf ball, the Z direction.

As discussed above, golf balls containing dimple patterns having a parting line about the equator may result in orientation specific flight characteristics. As mentioned above, the parting lines are desired by manufacturers for ease of production, as well as by many golfers for lining up a shot for putting or off the tee. It has now been discovered that selective design of golf balls with dimple patterns including a parting line meeting the aerodynamic criteria set forth in Table 7 result in flight distances far improved over prior art. Geometrically, these parting lines must be orthogonal with the axis of rotation. However, in one embodiment of the present invention, there may be a plurality of parting lines with multiple orientations.

Another way of achieving aerodynamic symmetry or correction for asymmetrical orientation is to use a dimple pattern that congregates a certain amount of relatively shallow dimples about the poles of the golf ball. In this regard, dimples having profiles based on equation (2) using the preferred ranges of chordal depth, diameter, and shape factor are believed to accomplish aerodynamic symmetry. In addition, it is contemplated that dimple profiles based on equation (2) and having chordal depths between about 0.002 inches to about 0.008 inches but not limited to any particular diameter or shaped factor may result in correction of asymmetry.

In another embodiment, asymmetry is overcome through the use of a staggered wave parting line as discussed earlier. For example, at least a portion or all of the dimples adjacent the parting line are aligned with and positioned to overlap corresponding dimples across the parting line.

While it is apparent that the illustrative embodiments of the invention herein disclosed fulfill the objectives stated above, it will be appreciated that numerous modifications and other embodiments may be devised by those skilled in the art.

For example, as used herein, the term "dimple", may include any texturizing on the surface of a golf ball, e.g., depressions and extrusions. Some non-limiting examples of depressions and extrusions include, but are not limited to, spherical depressions, meshes, raised ridges, and brambles. The depressions and extrusions may take a variety of planform shapes, such as circular, polygonal, oval, or irregular. Dimples that have multi-level configurations, i.e., dimple within a dimple, are also contemplated by the invention to obtain desirable aerodynamic characteristics. As such, while the majority of the discussion relating to dimples herein relates to those dimples having profiles based on a catenary curve, other types of dimples fitting the definition in this paragraph are contemplated for use in any portions of the golf ball surface not covered by dimples with catenary curve profiles.

Therefore, it will be understood that the appended claims are intended to cover all such modifications and embodiments which come within the spirit and scope of the present invention.

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What is claimed is:

1. A golf ball having a plurality of recessed dimples on the surface thereof, wherein at least a portion of the plurality of recessed dimples have a profile defined by the revolution of a catenary curve according to the following function:

$$y = \frac{d_c (\cosh(sf * x) - 1)}{\cosh\left(sf * \frac{D}{2}\right) - 1}$$

wherein y is the vertical direction coordinate away from the center of the ball with 0 at the center of the dimple;

x is the horizontal (radial) direction coordinate from the dimple apex to the dimple surface with 0 at the center of the dimple;

sf is a shape factor;

d_c is the chordal depth of the dimple;

D is the diameter of the dimple; and

wherein D is between about 0.115 inches and about 0.185 inches, sf is from about 5 to about 200, and d_c is from about 0.002 inches to about 0.008 inches.

2. The golf ball of claim 1, wherein at least a portion comprises about 50 percent or more of the dimples on the golf ball.

3. The golf ball of claim 1, wherein at least a portion comprises about 80 percent or more of the dimples on the golf ball.

4. The golf ball of claim 1, wherein D is between about 0.125 inches and about 0.185 inches.

5. The golf ball of claim 1, wherein sf is from about 10 to about 100.

6. The golf ball of claim 1, wherein sf is from about 10 to about 75.

7. The golf ball of claim 1, wherein d_c is from about 0.004 inches to about 0.006 inches.

8. The golf ball of claim 1, wherein D is between about 0.115 inches and about 0.185 inches, sf is from about 10 to 100, and d_c is from about 0.004 inches to about 0.006 inches.

9. The golf ball of claim 1, wherein the golf ball comprises a plurality of dimples having an aerodynamic coefficient magnitude defined by $C_{mag} = \sqrt{(C_L^2 + C_D^2)}$ and an aerodynamic force angle defined by $\text{Angle} = \tan^{-1}(C_L/C_D)$, wherein C_L is a lift coefficient and C_D is a drag coefficient, wherein the golf ball comprises:

a first aerodynamic coefficient magnitude between about 0.24 and about 0.29 and a first aerodynamic force angle between about 32 degrees and about 39 degrees at a Reynolds Number of about 230000 and a spin ratio of about 0.080; and

a second aerodynamic coefficient magnitude between about 0.24 and about 0.29 and a second aerodynamic force angle between about 33 degrees and about 41 degrees at a Reynolds Number of about 208000 and a spin ratio of about 0.090.

10. The golf ball of claim 9, further comprising:

a third aerodynamic coefficient magnitude between about 0.25 and about 0.30 and a third aerodynamic force angle between about 34 degrees and about 42 degrees at a Reynolds Number of about 190000 and a spin ratio of about 0.10; and

a fourth aerodynamic coefficient magnitude between about 0.25 and about 0.31 and a fourth aerodynamic force angle between about 35 degrees and about 43 degrees at a Reynolds Number of about 170000 and a spin ratio of about 0.11.

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11. A golf ball having a plurality of recessed dimples on the surface thereof, wherein at least a portion of the plurality of recessed dimples have a profile defined by the revolution of a catenary curve according to the following function:

$$y = \frac{d_c(\cosh(sf * x) - 1)}{\cosh\left(sf * \frac{D}{2}\right) - 1}$$

wherein y is the vertical direction coordinate away from the center of the ball with 0 at the center of the dimple;

x is the horizontal (radial) direction coordinate from the dimple apex to the dimple surface with 0 at the center of the dimple;

sf is a shape factor and from about 10 to about 75;

d_c is the chordal depth of the dimple and from about 0.004 inches to about 0.006 inches; and

D is the diameter of the dimple.

12. The golf ball of claim 11, wherein D is between about 0.115 inches and about 0.185 inches.

13. The golf ball of claim 11, wherein D is between about 0.125 inches and about 0.185 inches.

14. The golf ball of claim 11, wherein at least a portion comprises about 50 percent or more of the dimples on the golf ball.

15. The golf ball of claim 11, wherein at least a portion comprises about 80 percent or more of the dimples on the golf ball.

16. The golf ball of claim 11, wherein the golf ball comprises a plurality of dimples having an aerodynamic coefficient

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magnitude defined by $C_{mag} = \sqrt{(C_L^2 + C_D^2)}$ and an aerodynamic force angle defined by $\text{Angle} = \tan^{-1}(C_L/C_D)$, wherein C_L is a lift coefficient and C_D is a drag coefficient, wherein the golf ball comprises:

5 a first aerodynamic coefficient magnitude between about 0.24 and about 0.29 and a first aerodynamic force angle between about 32 degrees and about 39 degrees at a Reynolds Number of about 230000 and a spin ratio of about 0.080; and

10 a second aerodynamic coefficient magnitude between about 0.24 and about 0.29 and a second aerodynamic force angle between about 33 degrees and about 41 degrees at a Reynolds Number of about 208000 and a spin ratio of about 0.090.

15 17. The golf ball of claim 16, further comprising:

a third aerodynamic coefficient magnitude between about 0.25 and about 0.30 and a third aerodynamic force angle between about 34 degrees and about 42 degrees at a Reynolds Number of about 190000 and a spin ratio of about 0.10; and

a fourth aerodynamic coefficient magnitude between about 0.25 and about 0.31 and a fourth aerodynamic force angle between about 35 degrees and about 43 degrees at a Reynolds Number of about 170000 and a spin ratio of about 0.11.

18. The golf ball of claim 11, wherein the volume ratio is at least about 0.60.

19. The golf ball of claim 1, wherein the volume ratio is at least about 0.60.

* * * * *